Chapter 6
Reclamation and Management of Alkali Soils for Crop Production

6.1 Factors Affecting Plant Growth in Alkali Soils

Plant growth, yield and or quality of crops in alkali soils are affected by anyone and or combination of the following factors:

(i) Poor water and air permeability as a result of high dispersion of clay and silt particles and breakdown of soil aggregates (Richards 1954; Abu-Sharar et al. 1987).
(ii) Low availability of water due to shallow wetting zones, low water storage, poor internal conductance in the post-irrigation periods and restricted depth of roots (Acharya and Abrol 1975; Acharya et al. 1979; Sandhu et al. 1980).
(iii) Hard crust on surface which greatly hinders water infiltration, gaseous exchange and seedling emergence (Richards 1954; Allison and Moore 1956; McIntyre 1958; Moore and Singer 1990).
(iv) Difficulties in preparing seedbed as all the soil does not come to proper moisture conditions at the same time. This also results in clod formation and poor tilth of soil (Siyal et al. 2002).
(v) Deficiency of calcium since nearly all soluble and exchangeable-Ca^{2+} is precipitated as insoluble $CaCO_3$ (Chhabra and Abrol 1983).
(vi) Excess of Na^+ which is toxic *per se* to plants and causes imbalance nutrition due to antagonistic effect on K and Ca uptake (Singh et al. 1980a, b; Chhabra and Abrol 1983).
(vii) Toxic concentration of HCO_3^- and CO_3^{2-} anions which affect cell enzymatic activities (Miller and Evans 1956), root growth by adversely affecting cell elongation (Lee and Woolhouse 1969) and nutrient availability (Chhabra and Abrol 1983).
(viii) Toxic concentration of Al and Si: In alkali soils, due to hydrolysis and break down of clay minerals, there is high release of soluble Si and Al which cause toxicity to plants. Correns (1968) reported increase in SiO_2 solubility by a factor of 4.5 at pH 7.0 and by a factor of 6 at pH 10.0 as compared to its

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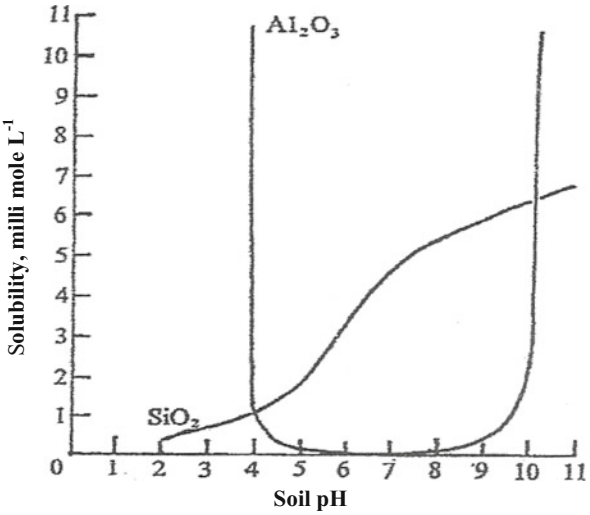

Fig. 6.1 Solubility of silica and alumina as a function of pH (Correns 1968)

solubility at pH 2.0. Al_2O_3 solubility is maximum both in acidic and alkaline pH range of soil (Fig. 6.1). Not only solubility, chemical forms of Al are also affected by soil pH (Brautigan et al. 2012). Hydroxyl forms of Al are more toxic than others. Al-toxicity to plants increases in the order of $Al(OH)_4^-$ > $Al(OH)_3$ > $Al(OH)_2^+$ > $Al(OH)^+$ > Al^{3+} (Vondrackova et al. 2015). But when bonded to sulphate, phosphate, silicates and fluorides, it becomes non-toxic. Toxic concentration of Al prevents elongation of roots, decreases lateral branches and encourages their thickening (Silva 2012). Such roots have low efficiency in absorbing nutrients and water. Excess-Al induces Fe-deficiency type symptoms in rice (Rout et al. 2001), wheat (Foy and Fleming 1982; Campbell and Lefever 1981) and sorghum (Furlani and Clark 1981). High concentration of Si affects the absorption of P and height of crops.

(ix) Increased solubility in soil (Chhabra et al. 1980a, b) and accumulation of toxic elements like F, B, Se and Mo in plants that may affect crop yield and or health of animals feeding on such crops. Increased concentration of F can cause severe problem of bone disease like "skeletal fluorosis" in animals and human-being. Selenium toxicity causes *Degnala* disease which adversely affects skin and hairs of animals. It is also called "alkali disease" (Arora 1985; Arora et al. 1975).

(x) Decreased solubility and availability of micro-nutrients like Zn, Fe, and Mn due to high pH, $CaCO_3$ and soluble CO_3^{2-} and HCO_3^- ions (Chhabra and Abrol 1983).

(xi) Low activity of useful microbes due to high pH and excess exchangeable-Na^+ (Bhardwaj 1975; Rao and Ghai 1985; Batra et al. 1997).

(xii) Presence of hard CaCO3 subsoil layer which acts as a physical barrier for movement of water, leaching of salts and vertical root growth of crops and trees (Chhabra et al. 1987; Chhabra and Kumar 1989; Chhabra 1991).

Table 6.1 Expected loss of soil productivity due to ESP in different soils

ESP	Expected loss in productivity, %	
	Alkali alluvial soils (Alfisols)	**Alkali Vertisols**
Up to 5	Nil	< 10
5–15	< 10	10–25
15–40	10–25	25–50
> 40	25–50	> 50

Source: Latha and Janki (2015)

Table 6.2 ESP and pHs of the soil and sodicity hazards to the plants

Approximate ESP	pHs	Sodicity hazards
< 15	< 8.2	Non to slight
15–35	8.2–8.4	Slight to moderate
34–50	8.4–8.6	Moderate to high
50–65	8.6–8.8	High to very high
> 65	> 8.8	Extremely high

Source: Chhabra (1996)

(xiii) Continuous loss of surface fertile soil by wind and water erosion due to low shear stress (Arulanandan and Heinzen 1977; Gupta 1982).

Due to increase in ESP, there is significant loss in productivity of soil (Table 6.1). Under field conditions, plant growth is adversely affected due to combination of the above factors, the extent depending upon level of ESP, pHs, nature and stage of crop growth, environmental conditions and the overall management levels. Approximate extent of sodicity hazards in relation to ESP and pHs of surface 15 cm soil for most of crop plants (Glycophytes) is given in Table 6.2.

The adverse effects of exchangeable-sodium on growth and yield of crops in various classes occur according to their relative tolerance to sodicity. Whereas growth and yield of sensitive crops are affected at ESP levels even below 15, only extremely tolerant native grasses can grow at ESP above 65 (Abrol et al. 1980).

6.2 Relative Tolerance of Crop to Soil ESP

Different crops vary widely in their tolerance to soil exchangeable-sodium. In general, cereals are more tolerant than legumes as they require less Ca, availability of which is a limiting factor in alkali soils. Those crops which can withstand excess moisture in root environment are also generally more tolerant to alkali conditions. Though the crop tolerance to soil sodicity varies with stage of growth, variety, environmental factors and level of management, their relative tolerance is summarized in Table 6.3.

Among cultivated crops, rice is most tolerant (Fig. 6.2a) to soil sodicity. It can withstand ESP up to 50 without any significant reduction in yield. It is followed by sugar beet and teosinte. Crops like wheat (Fig. 6.2b) barley and oats etc. are

Table 6.3 Relative tolerance of crops and grasses to soil ESP

Tolerant ESP 35–50	**Moderately tolerant ESP 15–35**	**Sensitive ESP < 15**
Karnal, *kallar* grass (*Leptochloa fusca*)	Wheat (*Triticum aestivum*)	Gram (*Cicer arietinum*)
Rhodes grass (*Chloris gayana*)	Barley (*Hordeum vulgare*)	Mash (*Vigna mungo*)
Para grass (*Brachiaria mutica*)	Oat (*Avena sativa*)	Chickpea (*Cajanus cajan*)
Bermuda grass (*Cynodon dactylon*)	Shaftal (*Trifolium resupinatum*)	Lentil (*Lens esculenta*)
Rice (*Oryza sativa*)	Alfalfa, lucerne (*Medicago sativa*)	Soybean (*Glycine max*)
Sesbania, *Dhaincha* (*Sesbania aculeata*)	Turnip (*Brassica rapa*)	Groundnut (*Arachis hypogaea*)
Sugar beet (*Beta vulgaris*)	Raya (*Brassica juncea*)	Sesamum (*Sesamum orientale*)
Teosinte (*Euchlaena mexicana*)	Sunflower (*Helianthus annuus*)	Mung bean (*Phaseolus aureus*)
	Mustard (*Brassica juncea*)	Pea (*Pisum saccharatum*)
	Sorghum (*Sorghum bicolor*)	Cowpea (*Vigna unguiculata*)
	Safflower (*Carthamus tinctorius*)	Maize (*Zea mays*)
	Egyptian clover, berseem (*Trifolium alexandrinum*)	Cotton (*Gossypium hirsutum*)
	Linseed (*Linum usitatissimum*)	
	Onion (*Allium cepa*)	
	Garlic (*Allium sativum*)	
	Pearl millet (*Pennisetum glaucum*)	
	Cotton (*Gossypium hirsutum*)	

Source: Chhabra (1996)

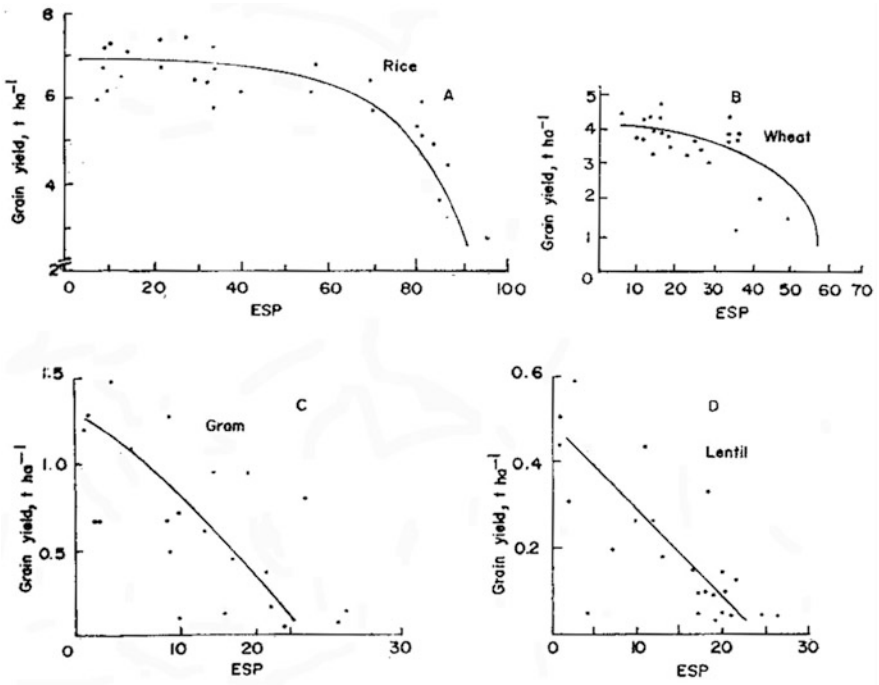

Fig. 6.2 (**a**–**d**) Effect of ESP on yield of crops (Abrol and Bhumbla 1979)

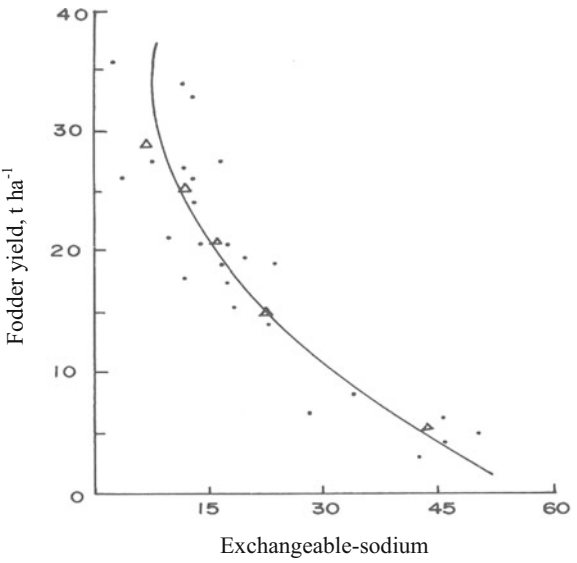

Fig. 6.3 Effect of soil exchangeable-sodium percentage on fodder yield of cowpea (Singh et al. 1980a, b)

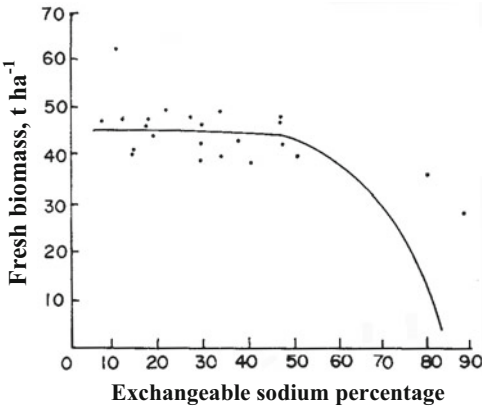

Fig. 6.4 Effect of ESP on fresh biomass of sesbania (Abrol and Bhumbla 1979)

moderately tolerant. Legumes like gram (Fig. 6.2c), mash and lentil (Fig. 6.2d), cowpea (Fig. 6.3) chickpea and pea etc. are very sensitive and their yield decreases significantly even when soil ESP is less than 15. *Sesbania* is an exception among the leguminous crops as it can withstand ESP up to 50 (Fig. 6.4) without any significant reduction in yield. Due to this it is an excellent choice for green manuring in alkali soils.

Among oilseed crops, except groundnut, all are moderately tolerant to soil ESP. However, raya followed by sunflower is more tolerant than others. Relative tolerance to soil ESP among green fodder crops decreases in the order of: teosinte < oats < shaftal < lucerne < turnip < berseem. Cotton is sensitive to soil sodicity at germination stage and suffers from "bad opening" of bolls at maturity, resulting in poor quality of fibre and difficulty in collecting the lint (Chhabra 1996). In case of pearl millet, crop raised in alkali soils through transplanted seedlings gives higher yields than the one raised through directly sowing seeds in field. This is due to its poor germination as a result of soil crust, and water stagnation during early stages of growth (Singh and Joshi 1988).

Some of forage grasses like Karnal grass (*Leptochloa fusca*) and Rhodes grass (*Chloris gayana*) are very tolerant to soil sodicity and in fact grow naturally under high alkali conditions (Ashok Kumar and Abrol 1986). Karnal grass not only tolerates but likes both surface waterlogging and high ESP in its growing environment. Most of sugarcane genotypes are sensitive to moderately tolerant to soil sodicity (Dang et al. 1998).

On the basis of earlier studies (Bernstein and Pearson 1956; Pearson and Bernstein 1958), Pearson (1960) listed crops according to their relative tolerance to soil ESP (Table 6.4). A careful comparison of the list in Table 6.4 with that in Table 6.3 brings out wide variations in the observed relative tolerance of some crops to ESP. This is mainly due to the fact that:

(a) The results of Pearson were based on experiments conducted in pots / lysimeters with soils whose structure had been stabilized with substances like Krilium or other soil conditioners so as to minimize soil physical problems, a situation which is practically not possible under field conditions.
(b) In Table 6.3 rice is rated as tolerant while in Table 6.4 it is rated as moderately tolerant. This is mainly because Pearson used seeded-rice while work done in India refers to the transplanted rice.
(c) The results obtained in pots under controlled conditions are affected by given uniform ESP of soil while under field conditions, ESP of the lower layers also influence crop performance. Thus, it is the combined effect of rootzone sodicity rather than a single ESP level that determines the relative tolerance of crops under field conditions.

Based on relative tolerance of crops, their reclaiming effect on soil, economic returns and climatic conditions of the area, it has been observed that rice – wheat – sesbania and rice – berseem (*Egyptian clover*) are the best sequences for cropping alkali soils in the initial 3 to 5 years. When pH of surface soil comes down i.e. between 8.5 and 9.0, then it is possible to adopt cropping patterns with relatively moderate tolerant crops. These include rice -barley, rice – mustard, sesbania – rice – sugar beet, sesbania – sugarcane – cotton etc. After 8–10 years of reclamation, all crops including vegetables, fruits, flowers, medicinal plants and high value industrial crops can be grown in these soils.

Table 6.4 Tolerance of various crops to exchangeable-sodium percentage under amended physical conditions

Tolerance to ESP and range at which affected	Crops	Growth response under field conditions
Extremely sensitive, ESP = 2–10	Deciduous fruits, nuts, Citrus spp. Avocado (*Persea americana*)	Sodium toxicity symptoms even at low ESP values.
Sensitive, ESP = 10–20	Beans (*Phaseolus vulgaris*)	Stunted growth of crop at these ESP values even though the physical conditions of the soil may be good.
Moderately tolerant, ESP = 20–40	Clover (*Trifolium* spp.) Oats (*Avena sativa*) Tall fescue (*Festuca arundinacea*) Rice (*Oryza sativa*) Dallisgrass (*Paspalum dilatatum*)	Stunted growth due to both, nutritional factors and adverse soil physical conditions.
Tolerant, ESP = 40–60	Wheat (*Triticum aestivum*) Alfalfa (*Medicago sativa*) Barley (*Hordeum vulgare*) Tomatoes (*Lycopersicon esculentum*) Garden beet (*Beta vulgaris*)	Stunted growth usually due to adverse physical conations of soil.
Most tolerant, ESP > 60	Crested and fairway wheat grass (*Agropyron* spp.) Tall wheatgrass (*Agropyron elongatum*) Rhodes grass (*Chloris gayana*)	Stunted growth usually due to adverse physical conations of soil.

Source: Pearson (1960)

6.3 Reclamation of Alkali Soils

Cropping of alkali soils presents difficulties due to their poor physical, chemical and biological properties which affect seedbed preparation, choice of crops, fertilizer and irrigation practices, drainage and other field operations. Reclamation involves amending these properties so as to provide optimal environment for maximum crop production.

6.3.1 Reclamation Technologies

Generally, "one-size-fit-all" model of reclamation does not exist. Based on local soil conditions, technical and economic feasibilities, and social involvement of the stockholders, one has to pick and choose and mix various components of different technologies to achieve maximum results. Alkali soils can be reclaimed by any of the following technologies.

6.3.1.1 Biological Reclamation

Reclamation of alkali soils is primarily a chemical process in which exchangeable-sodium is replaced with calcium (Eq. 6.1) to lower ESP and pH. In biological reclamation, also referred as **bioremediation, phytoremediation, vegetative amelioration** and **plant-assisted reclamation**; the soluble calcium required for replacing exchangeable-Na^+ is provided by dissolving native $CaCO_3$ (Eqs. 6.2 and 6.3) through (a) the use of biological CO_2 produced by the respiration of growing plant roots and decomposition of organic materials, and (b) enhanced leaching through improvement in soil physical properties.

$$\underset{\text{Alkali soil}}{Na^+\text{-soil}} + \underset{\text{Soluble calcium}}{Ca^{2+}} \rightarrow \underset{\text{Good soil}}{Ca^{2+}\text{-soil}} + \underset{\text{To be leached down}}{NaCO_3 \downarrow} \tag{6.1}$$

$$\underset{\text{Native form the soil}}{CaCO_3} + \underset{\text{Biological}}{CO_2} + H_2O \rightarrow \underset{\text{Partially soluble}}{Ca(HCO_3)_2} \tag{6.2}$$

$$\underset{\text{Formed in situ}}{Ca(HCO_3)_2} + \underset{\text{Alkali soil}}{2Na^+\text{-soil}} \rightarrow \underset{\text{Good soil}}{Ca^{2+}\text{-soil}} + \underset{\text{To be leached down}}{2NaHCO_3 \downarrow} \tag{6.3}$$

This was one of the indigenous methods of *usar* soil reclamation adopted by the farmers in Oudh region in Uttar Pradesh, India (Moreland 1901). Even today, many farmers reclaim their alkali soils by simply tilling the land, ponding water, addition of rice husk, rice and wheat straw, FYM, and or by growing local salt-tolerant rice varieties without or with very low doses of chemical amendments.

Biological reclamation can be divided into two modules one for reclaiming soils for crop production and the other for reclaiming soils for sustaining natural vegetation and ecological balance of the area.

In Hungary, deSigmond (1924) reclaimed irrigated, heavy black alkali soils (Vertisols) at Bekescsaba Experimentation station, by growing a mixture of different grasses and legumes. Kelley and Brown (1934) on a fine sandy loam sodic soil (ESP 57–67, pH 9.2–9.7, $EC_{1:5}$ 6.1–7.2 dS m^{-1} of 0–30 cm soil) located on the Kearney Ranch Farm near Fresno, California, USA, observed that after 10 years of copping which included, 1 year of flooding, 1 year of barley cultivation, 7 years of green manuring, [2 years with Indian sweet clover (*Melilotus indicus*) and 5 years with alfalfa (*Medicago sativa*)] followed by 1 year of fallow, the yield of cotton, the first post-reclamation crop, was 1.82 t ha^{-1} for the gypsum treated plots against the yield of 2.10 t ha^{-1} from the plots where gypsum was not added and considered as phytoremediation treatment (Table 6.5). The plots were kept flooded for 3 weeks by repeated application of well water (ECiw 0.3 dS m^{-1}, SAR 0.7). They attributed this to the improvement in soil properties due to cultivation of crops and green manuring and called this as phytoremediation of sodic soils. Even better results were obtained when Bermuda grass (*Cynodon dactylon*) was used as first phytoremediation crop in the sequence (Kelley 1937). However, in these experiments, no information is available on yield of different crops during first 9 years. At

Table 6.5 Improvement in soil properties as affected by application of gypsum alone and in combination with cropping after 10 years

	Soil properties, ESP			
	Gypsum[a] + Cropping[b]		Cropping alone[b]	
Soil depth, cm	Initial	Final	Initial	Final
0–30	70	5	65	6
30–60	67	8	70	21
60–90	54	9	46	26
90–120	35	19	28	53
Mean ESP for 120 cm soil depth	49	10	52	27
Cotton yield after 10 years	1.82		2.10	

Source: Kelley (1937)
[a]Gypsum application @ 37 Mg ha^{-1} in two splits: 22 Mg in the year 1920 and 15 Mg in the year 1921
[b]Cultivation of barley for 2 years, green manuring by clovers for 2 years, and alfalfa grown for 5 years

Table 6.6 Effect of growing rice crop on improvement in soil ESP, pH and removal of Na^+(me) form a highly alkali soil

Original soil		Without rice		With rice		Excess Na^+ removed by growing rice
$pH_{1:2}$	ESP	$pH_{1:2}$	ESP	$pH_{1:2}$	ESP	
10.3	93.3	9.6	68.6	8.9	28.6	163
9.5	46.0	8.9	26.3	8.3	1.2	80
9.0	29.9	8.4	9.5	8.2	0.6	19
8.4	10.5	8.1	1.8	7.2	0.2	3

Source: Chhabra and Abrol (1977)

the same time no information is available on the yearly improvement in soil properties.

Using alluvial soil of different ESP (Table 6.6) but same mineralogy and $CaCO_3$ content, Chhabra and Abrol (1977) observed high degree of improvement in soil pH_2 and ESP under treatment with rice as compared to those without rice plants. Further, net Na^+ removal was more at high ESP and was attributed to the biological action of rice roots. As compared to those from the treatment without rice plant, pH of the percolate was significantly low and HCO_3^- content more from than those treatments with rice plants. Both these factors increased solubility of native $CaCO_3$ and helped in lowering soil ESP.

Qadir et al. (2003b) on a moderately alkali soil (pHs 7.2, SAR 15.9, ECe 4.9 dS m^{-1}, $CaCO_3$ 5%) observed more removal of Na^+ from gypsum and alfalfa treatments as compared to the control plots. Similar reclamation was achieved when alkali soils were cultivated with grasses (Ashok Kumar and Abrol 1986) and planted with trees like *Sesbania* (Chhabra et al. 1987) and *Prosopis juliflora* (Singh and Gill 1992).

Biological reclamation ($BioR_{alkali}$) involves the following mechanisms and processes:

$$\mathrm{BioR_{alkali}} = \mathrm{R_{pCO2}} + \mathrm{R_{H+}} + \mathrm{R_{phy}} + \mathrm{R_{ImNa+}} + \mathrm{S_{Na+}} \quad (6.4)$$

Where $\mathrm{BioR_{alkali}}$ refers to the extent of reclamation achieved through bioremediation; $\mathrm{R_{pCO2}}$ refers to reclamation due to increase in partial pressure of CO_2 in the rhizosphere as a result of respiration of plant roots and decomposition of OM; $\mathrm{R_{H+}}$ refers to reclamation due to enhanced proton (H^+) release by plant roots in the rhizosphere; $\mathrm{R_{phy}}$ refers to improvement in soil physical properties like infiltration rate, hydraulic conductivity and soil aggregation; $\mathrm{R_{ImNa+}}$ refers to immobilization of soluble Na^+ by organic complexes in soil and $\mathrm{S_{Na+}}$ refers to the amount of Na^+ removed through harvest of plant parts (adopted from Qadir and Oster 2002; Qadir et al. 2007).

In soil, CO_2 is produced due to respiration of plant roots, decomposition of OM, and biological activities of soil macro-organisms. Due to this, its concentration increases from 0.04% (in the atmosphere) to about 0.4% in soil air. In well-aerated soils, under dry conditions, there is a good exchange between soil and atmospheric air due to which CO_2 of soil keeps on diffusing to atmospheric air and thus a dynamic balance is maintained preventing its accumulation in the rhizosphere. But on waterlogging, the soil pores get blocked preventing its escape to the atmospheric air. Under such situations its concentration increases even up to 1% (Nelson and Oades 1998). In saturated and waterlogged soils, and in soils with low atmospheric exchange as in alkali soils, most of the biological CO_2 is retained in soil itself with manifold increase in pCO_2. These elevated pCO_2 lead to the higher production of H_2CO_3 which then reacts with insoluble $CaCO_3$, already present in soil and dissolves it to provide soluble Ca^{2+} for replacement of soil exchangeable-Na^+. Robbins (1986a) measured pCO_2 in the rootzone of several crops during amelioration of a calcareous alkali soil (pHs 8.6, ESP 33, ECe 2.4 dS m^{-1}). The pCO_2 values fluctuated during crop growth and were maximum during vigorous / active growth period. These were higher from cropped than from the un-cropped treatments. Among the different crops tried, pCO_2 developed and Na^+ removal was maximum under Sudan grass, a cross between *Sorghum bicolor* and *S. drummondii,* which is a fast-growing fodder crop. These results (Robbins 1986b, Table 6.7) showed that crops like Sudan grass can be as efficient as gypsum in reclaiming alkali soils.

In a modelling study, Simunek and Suarez (1997) predicted that biological amelioration of sodic soils containing calcite was feasible, but the time and quantity of water required for amelioration to increase pCO_2 to 2 kPa (1 kPa = 1% CO_2) to enhance dissolution of calcite was approximately two times greater than that required for amelioration with gypsum.

Release of H^+ from plant roots in exchange for absorption of cations from soil is considered as the major process contributing to decrease in pH of the rhizosphere. Several studies have shown that various plant species supplied with ammonium (NH_4^+) as a source of N, acidify their rhizosphere, whereas the same species alkalize it when nitrate (NO_3^-) is supplied as a source of N (Marschner and Romheld 1983). In general, roots of leguminous plants produce more acidity than the non-leguminous plants. These also have the advantage of increasing soil N-fertility

Table 6.7 Mean values of net Na^+ removal from alkali soil as a function of pCO_2 in the rootzone of different crops raised in lysimeters

Treatments	Range of pCO_2 kPa produced during the experimental period	Na^+ removed, mol lysimeter^{-1}
Control (without gypsum, without crop)	0.9–4.9	1.0 ± 0.1
Gypsum alone[a] (without crop)	2.0–12.5	5.6 ± 0.3
Manure alone[b] (without crop)	1.0–4.9	1.6 ± 0.1
Green-manure[c]	2.0–12.5	4.7 ± 0.2
Cotton (*Gossypium hirsutum*)	1.8–8.5	1.4 ± 0.1
Alfalfa (*Medicago sativa*)	2.0–14.0	4.6 ± 0.2
Soudan grass (*Sorghum bicolor*)	2.5–18.5	10.1 ± 0.3

Source: Extracted from the graphs of Robbins (1986a, b)
[a]Gypsum applied @ 5 kg m^2 i.e. 50 t ha^{-1} and incorporated in the surface 0–2 cm soil
[b]Fresh manure applied @ 5 kg m^2 i.e. 50 t ha^{-1} and incorporated in the surface 0–2 cm soil
[c]Fresh chopped alfalfa @5 kg m^2 i.e. 50 t ha^{-1} applied as GM and incorporated in the surface 0–2 cm soil

Table 6.8 Effect of N-application on the shoot and root dry matter production and Na^+ removal by alfalfa (*Medicago sativa*)

Treatments	Biomass produced, g lysimeter^{-1}		Na^+ removed, m mol lysimeter^{-1}
	Shoot	Root	
N_2-fixing alfalfa, inoculated with rhizobium (*rhizobium meliloti*) strain no. 6052.	31.2 ± 0.9[a]	12.0 ± 0.3a	26.1 ± 0.4a
NH_4NO_3 –fed alfalfa, supplied with mineral-N (100 mg kg^{-1} soil at sowing +50 mg kg^{-1} soil 12 days after sowing).	30.2 ± 0.3a	11.2 ± 0.1a	24.2 ± 0.5b

Source: Qadir et al. (2003b)
[a]Means followed by the same letter within a column are not statistically different (P = 0.05)

through fixation of atmospheric nitrogen. Qadir et al. (2003b) evaluated alfalfa (*Medicago sativa*) without N supplement (relying on N_2-fixation) with that dependent on ammonium treatments, which produced statistically similar root and shoot biomass, but there was 8% greater removal of Na^+ in the leachate collected from the soil columns grown with N_2-fixing alfalfa (Table 6.8). That indicated dissolution of an additional amount of calcite in the N_2-fixing treatment, suggesting that the amelioration rate of calcareous alkali soils could be increased by means of crop management conducive for release of greater amount of CO_2 and H^+ in the rootzone (Qadir et al. 2003a). Bauder and Brock (2001) concluded that C3 (grass-type) crops, which consume relatively significant amounts of atmospheric-CO_2, facilitated

leaching of Na^+ as a consequence of higher acidification of soil solution. But except sesbania and alfalfa, legumes are less tolerant to soil sodicity and surface waterlogging and thus are not ideal choice for bioremediation of alkali soils. Further, due to buffering capacity of soil, pH changes in vicinity of roots (Rhizosphere) do not necessarily bring substantial changes in bulk of soil.

Plant roots also play an important role in facilitating the process of leaching Na^+, replaced from soil exchange complex, and CO_3^{2-}, HCO_3^- and other reaction products, to deeper soil layers by providing living channels for movement of water (Chhabra and Abrol 1977) and by improving soil physical properties. Continuous cultivation of Karnal grass (*Diplachne fusca*) improved chemical and physical properties (Table 6.9) of alkali alluvial soils (Kumar and Abrol 1984; Ashok Kumar et al. 1994; Akhtar et al. 2004).

Plant roots improve soil porosity by creating biopores and structural cracks (Czarnes et al. 2000; Yunusa and Newton 2003). In addition, roots stimulate changes in the rhizosphere through removal of entrapped air from larger conducting pores and by generating alternate wetting and drying cycles. Aggregate stability is also enhanced because of in situ production of polysaccharides and fungal hyphae in conjunction with differential dewatering at the root-soil interface (Tisdall 1991). Roots of some crops act like a potential tillage tool as they can grow through compacted soil layers and improve soil below the plough pan (Elkins et al. 1977). Roots of alfalfa (Akhter et al. 2004), and grasses like Karnal grass (Malik et al. 1987), Bahia grass (P*aspalum notatum*) and tall fusca (*Festuca arundinacea*) can

Table 6.9 Effect of growing *Kallar* grass (*D. fusca*) continuously on physical and chemical properties[a] of a highly alkali soil

Treatments	pHs	ECe, dS m^{-1}	ESR	OM, g kg^{-1} soil	Available water, kg kg^{-1} soil	Bulk density, mg m^{-3}	Porosity, %	Ks, mm day^{-1}
Control	10.4	22.0	185.5	3.3	0.155	1.62	38.9	0.04
Kallar grass after 1 year	9.3	12.6	70.6	3.2	0.175	1.61	39.1	1.5
Kallar grass after 2 years	9.1	7.4	65.9	5.5	0.184	1.58	40.4	9.0
Kallar grass after 3 years	9.2	3.2	32.5	7.3	0.195	1.55	41.5	18.0
Kallar grass after 4 years	9.1	2.8	25.8	6.3	0.216	1.54	42.3	38.0
Kallar grass after 5 years	8.9	2.0	20.7	7.4	0.214	1.53	42.8	55.6

Source: Akhtar et al. (2004)
[a]Surface 20 cm soil

penetrate the soil to a depth of 1 m. These deep penetrating roots, on decay provide channels for water and air movement and leaching of salts through otherwise compacted subsoil layers. Further, with increase in hydraulic conductivity due to penetration of roots, more water passes through the soil leading to increased solubility of $CaCO_3$. But significant increase in Ca^{2+} solubility cannot be explained only by simple hydrolysis of $CaCO_3$. *Sesbania* roots are though thick and well branched, but grow only to a shallow depth. Chhabra et al. (1987) observed that roots of *Sesbania* species (*Sesbania aegyptiaca*, *Sesbania formosa* and *Sesbania sesban*) did not have enough penetrating power to cross the hard-compact subsoil layer of alkali soils. Even increasing the root volume by increasing the number of plants per hole from one to three, Ses*bania* roots could not cross the compact layer present at depth of 60 cm. Indian mustard, canola (*Brassica napus*) and cotton though have deep tap root system, these do not penetrate to deeper depths as compared to the roots of alfalfa. Cresswell and Kirkegaard (1995) suggested that to improve porosity of compact subsoil layers like that in duplex alkali soils, crops like alfalfa should be included in mixed cropping system.

In case of reed and Bahia grass, their strong, long and fibrous rhizomes like stolons (runners) which root at nodes to form new plants, can open up or loosen the heavy textured soils and increase permeability (Bakker and Biewiga 1957). The roots of some trees like mesquite and *peepal* (*Ficus religiosa*) can act as a potential tillage tools referred as "biological drilling" by penetrating the dense subsoil layers.

Biological reclamation is faster under grasses, and a combination of grasses with trees than under trees alone. This is due to their intensive root activities and bio-harvesting of salts, which is achieved by removing the above ground parts (used as fodder) from the field. On the contrary, foliage of trees falls on the ground within the field and when this forest litter decomposes, it releases the absorbed salts back in the soil itself.

Decrease in salt concentration of soil (S_{Na+}) through removal by the aboveground parts of most cultivated crops, which are primarily glycophytes, is insignificant as compared to the total quantity of salts present in soil. Considering the biomass produced (i.e. the above ground yield) and salt concentration in the tissue, even the forage crop like alfalfa is able to remove 1–2 t ha^{-1} of salts only. The estimates of Gritsenko and Gritsenko (1999) reveal that Na^+ uptake by aboveground biomass of several plant species constitutes 2–20% of the total salt uptake (Table 6.10) which makes a very small fraction of the total Na^+ present in alkali soils. Hence, the principal mechanisms of decrease in soil sodicity through continuous cultivation of crops is through higher solubility of $CaCO_3$ and higher leaching of the replaced Na^+ out of the effective rootzone, rather than removal by bio-harvesting of the aboveground parts.

Field experiments have revealed that except time taken, chemical amelioration and bio-reclamation approaches perform similarly in terms of their ability to decrease soil sodicity levels. Results of a field experiment (Kumar and Abrol 1984) conducted on a *barren*, calcareous, alkali soil ($pH_{1:2}$ 10.6, $EC_{1:2}$ 2.7 dS m^{-1}, ESP 94) indicated that the amelioration efficiency of two grasses, Para grass (*Brachiaria mutica*) and Karnal grass, was comparable with soil application of

Table 6.10 Phytoextraction of Na^+ by some plant species

Plant species	Shoot dry matter, t ha^{-1}	Salts removed, kg ha^{-1}	Na^+ removed, kg ha^{-1}
Japanese millet (*Echinochloa esculenta*)	8.2	224	46
Amaranth (*Amaranthus cruentus*)	5.0	182	3
Sunflower (*Helianthus annuus*)	9.1	172	4
Sudan grass (Sorghum × drummondii)	5.0	71	
Alfalfa (*Medicago sativa*)	11.3	178	26

Source: Gritsenko and Gritsenko (1999)

Table 6.11 Yield of rice and wheat as affected by application of gypsum and cultivation of grasses for one and 2 years in a highly alkali soil of the Indo-Gangetic region, India

Treatments	Rice yield, t ha^{-1}	Wheat yield, t ha^{-1}
Rice – wheat, without gypsum	00	00
Rice – wheat, with gypsum @ 12.5 t ha^{-1}	3.70	2.60
Rice – wheat followed by Para grass grown for I year without gypsum	3.80	0.13
Rice – wheat followed by Para grass grown for 2 year without gypsum	5.30	2.56
Rice – wheat followed by Karnal grass grown for 1 year without gypsum	4.10	0.26
Rice – wheat followed by Karnal grass grown for 2 year without gypsum	6.10	3.41

Source: Kumar and Abrol (1984)

gypsum @ 12.5 t ha^{-1} (Table 6.11) after 1 year of reclamation. Grain yield of first rice crop in the gypsum treatment averaged 3.7 t ha^{-1} as compared to 3.8 and 4.1 t ha^{-1} from the treatments cropped for 1 year with Para and Karnal grasses, respectively. The corresponding rice yields after 2 years of grass cultivation were even higher i.e. 5.30 and 6.10 t ha^{-1} respectively. Yield of wheat after 2 years of cultivation with Karnal grass was also better than in gypsum application alone.

In alkali soils, where pH_2 was >10, yield of rice grown as first crop and the following wheat, in treatment without application of gypsum was nil. This is because rice is less tolerant to sodicity as compared to Karnal grass, Rhodes grass, Para grass and Bermuda grass (Chhabra 1996; Table 6.3). Qadir et al. (1996) compared four forage crops *viz*. Karnal / Kallar grass, sesbania (*Sesbania bispinosa*), millet rice (*Echinochloa colona*) and finger millet (*Eleusine coracana*) against a control and a non-cropped gypsum @ 14.8 t ha^{-1} treatment for their capacity to ameliorate a calcareous, medium-textured, alkali soil (pHs = 8.6 ± 0.2, ECe = 10.3 ± 0.7 dS m^{-1}, SAR = 66 ± 6). The effectiveness of these in lowering SAR was in the order of gypsum > sesbania > Karnal grass > millet rice > finger millet > control. The forage

Table 6.12 Performance of different forage crops and their capacity to decrease SAR of an alkali soil

Treatments/Forage crop	Forage yield, t ha^{-1}	Decrease in SAR
Control (no gypsum, no crop)	–	12.8
Gypsum alone, @ 14.8 t ha^{-1}	–	37.8
Sesbania (*Sesbania bispinosa*)	32.3	32.5
Karnal (Kallar) grass (*Leptochloa fusca*)	24.6	29.1
Millet rice (*Echinochloa colona*)	22.6	23.4
Finger millet (*Eleusine coracana*)	5.4	17.9

Adopted from Qadir et al. (2003b)

yield of each species was directly proportional to the subsequent reduction observed in SAR of soil (Table 6.12).

Efficiency of biological reclamation depends upon balance between two opposite processes. The first is production of CO_2 mainly through respiration of plant roots and decomposition of OM, which is maximum under aerobic, unsaturated conditions. The second is trapping of the produced CO_2 in soil water to form H_2CO_3 which in turn increases solubility of native $CaCO_3$. The second process is maximum under saturated and waterlogged conditions which itself leads to anaerobic situations adversely affecting the fist process.

Hence, one needs crops like sesbania, rice, alfalfa or natural vegetation like Karnal grass, Bermuda grass and Sudan grass which can tolerate surface waterlogging, produce high amounts of CO_2 through root respiration and also tolerate high soil ESP. Contrary to the suggestion made by Qadir et al. (2007), other crops which though may tolerate relatively moderate to high ESP but require upland conditions for their growth, are less effective for this purpose. At the same time instead of continuous ponding, one should restore to a cycle of waterlogging and aerobic conditions (i.e. moisture level near field capacity) to maximize decomposition of OM and trapping of CO_2 within soil to solubilize native calcite. Further, to achieve reclamation on sustainable basis, it is important to leach down the replaced Na^+ from the rootzone. Leaching of reaction products by applying excess water (availability of which is a serious concern under arid conditions) and when the crop is in the field, is not safe for upland crops. Because in alkali soils this can lead to water stagnation, decrease in root aeration and lodging of crop causing low yields.

Biological reclamation is more effective for moderate alkali soils and or when used in combination with lower doses of chemical amendments. Under these situations, the plants can withstand the ambient soil sodicity and produce sufficient biomass to remove salts and enough root activities to dissolve native calcium carbonate. In highly alkali soils, when most plants are not able to grow and put up enough root and shoot biomass, bioremediation becomes ineffective. Since, biological reclamation is slow, the soil remains high in pH and ESP for long periods. It results in leaching losses of nutrients like P and K (Chhabra et al. 1980b) and movement of dispersed clay from surface to lower layers affecting physical properties and the capacity of soil to supply nutrients.

However, bioremediation technique as compared to chemical amelioration, improves soil biological health by increasing soil organic carbon, microbial biomass and microbial activity. This is achieved through addition of organic carbon from crop residues, sequencing of atmospheric-C, fixation of atmospheric-N and recycling of nutrients from lower to surface layers. Though Karnal grass is not a leguminous plant, Zafar et al. (1986) reported presence of diazotrophs in the inner cells indicating the presence of nitrogenase activity associated with its roots. Diazotrophs are free-living bacteria and archaea that fix atmospheric nitrogen gas as ammonia for use of plants. Archaea are single cell microorganisms which are similar to bacteria in size and simplicity of structure but radically different in molecular organization. These organisms like *Rhizobia* and Frankia (in symbiosis) and *Azospirillum* are able to grow without external sources of fixed nitrogen. A nitrogen fixing bacterium *Azoarcus olearius* has been found in endophytic compartments (inside the plant between the living cells in the roots of *L. fusca* (Malik and Zafar 1985). Reinhold-Hurek et al. (1993) reported the presence of *Azoarcus indigens and Azoarcus communis* species in the roots of *L. fusca*. Studies using the ^{15}N isotope dilution technique have also provided evidence of N conservation by Karnal / *Kallar* grass (Malik et al. 1987).

Batra et al. (1997) determined dehydrogenase activity (DHA), as a measure of catabolic activity of micro-organisms under anaerobic conditions, and microbial biomass carbon (MBC) of an alkali soil ($pH_2 = 10.6$, $EC_2 = 2.1$ dS m^{-1}, ESP = 95, DHA = 4.5 μg triphenylformazan (TPF) per g soil, MBC = 56.7 mg kg^{-1}) after various combinations of phytoremediation and chemical treatments consisting of Karnal grass grown alone for 1 or 2 years (harvested biomass removed or left to decompose on the soil surface), gypsum application (@14 t ha^{-1} alone, Karnal grass + gypsum, gypsum + sorghum, gypsum + rice and gypsum + sesbania. After 10 months, average DHA was 49.5 μg TPF per g soil in treatments where the soil was reclaimed by growing Karnal grass, compared with 26.8 μg TPF by applying gypsum. The levels of DHA after 3 years of reclamation were also greater (118.7 μg TPF per g soil) in the phytoremediation treatments than gypsum alone (96.1 μg TPF per g soil). The MBC values were however, greater in gypsum + crop treatments (206.3 mg kg^{-1} soil) as compared with Karnal grass treatments (161.7 mg kg^{-1} soil). In an earlier study, Rao and Ghai (1985) reported that permanent vegetation such as grasses, caused significant increases in urease and dehydrogenase activities in alkali soils. During decomposition of organic materials, soil microbes also release a variety of cementing substances of polysaccharide nature (Murayama 1984) which on drying act as strong binding agents holding particles together as water stable aggregates (Chanay and Swift 1984) and thus improve soil structure.

Biological reclamation though slow, is a viable option for small farmers having meagre resources and under situations when amendments are not easily available. This approach when used in combination with chemical reclamation helps in reducing the amount of chemical amendments and thus the cost of chemical reclamation. But in modern times when farmers have to buy large amounts of organic amendments from outside, it is not economical. As compared to chemical reclamation, biological reclamation is also less cost-effective. Though in biological

reclamation, one may save on cost of chemical amendments, other basic expenditure such as costs of field preparation, provision of irrigation (cost of installing tube well), seed / seedlings, fertilizers, insecticides, rent of land and labour remain the same for both biological and chemical reclamation. But yields of crops and saleable products in the initial 2–3 years of biological reclamation are significantly low as compared to those under chemical reclamation.

Generally, it is argued that availability of mined gypsum is limited and if the subsidy component is removed, chemical reclamation will become very costly and beyond the reach of farmers. But one should note that the availability of industrial gypsum such as phospho-gypsum, a by-product of fertilizer industry; flue gas desulphurization (FGD) gypsum, a by-product of coal-based power plants; sulphur, a by-product of petrochemical industry; and press mud, a by-product from sugarcane industry is increasing, and can be effectively used for reclamation of alkali soils.

6.3.1.2 Agro-Hydrological Reclamation

Agro-hydrological reclamation aims at reclaiming alkali soils through better water management at the local level. In many alkali soils, presence of hard impervious $CaCO_3$ layer causes surface waterlogging and shallow perched water table. In such situations simply puncturing the hard layer to let the standing water seep into deep layers, solves the problem. When the quality of groundwater is good, installation of shallow cavity tube wells which act as vertical drainage and also provide groundwater for irrigation of crops and augmentation of canal water supply, is the best solution. In areas where formation of alkali soils is due to shallow groundwater of high RSC as in Sharda Sahayak Command Area in U.P. and in some parts of Rajasthan and Haryana, India and many parts of the world, reclamation can be achieved simply by lowering water table by installation of shallow cavity tube wells and thereby cutting the source of $NaHCO_3$ and Na_2CO_3 coming to surface where they cause sodification of the effective rootzone. However, in these cases, farmers have to regularly treat high RSC groundwaters to reduce their adverse impact on soil properties and crop growth. Also, small amounts of chemical amendments have to be applied to lower down initial ESP of soil.

6.3.1.3 Chemical Reclamation

In this method, chemicals are used which directly add soluble-Ca^{2+} from outside or produce acid to dissolve native $CaCO_3$ and thus supply calcium in situ to replace exchangeable-Na^{+} and lower ESP of soil (Eq. 6.1).

6.4 Chemical Reclamation Technology

The major component of chemical reclamation technology recommended for commercial utilization of alkali soils is based on application of amendments and adoption of a package of cultural practices. Amendments are materials which i) directly supply soluble-Ca^{2+} exogenously to soil; or ii) indirectly supply Ca^{2+} by dissolving calcite (natively found in alkali soils), due to their acidulating effect.

Though alkali soils in arid and semi-arid regions contain both amorphous and precipitated $CaCO_3$ and many Ca-containing minerals, yet these do not directly help in reclamation. This is due to high pH of alkali soils where solubility of calcite (0.0006 g L^{-1} at 20 °C) is practically negligible. Kelley (1937) found no beneficial effect of applying grounded lime ($CaCO_3$) on reclamation of black alkali soils. During weathering process, Ca-bearing minerals cause super saturation of Ca in albite ($NaAlSi_3O$) leading to formation of anorthite ($CaAl_2Si_2O$), a derivative of plagioclase feldspar. Plagioclase series is a group of feldspar minerals which essentially have the same formula but vary in their percentage of Na and Ca. e.g. albite with (0% Ca) and anorthite with (90–100% Ca). Hydrolysis of these metastable Ca-containing minerals may release some soluble calcium (Suarez and Rhoades 1982; Eq. 6.5). However, that is not of much help as at high pH and in the presence of CO_3^{2-} and HCO_3^{-}, it gets precipitated as secondary calcium carbonate (Eq. 6.6).

$$\underset{\text{Anorthite}}{CaAl_2Si_2O_8} + nH_2O \xrightarrow{\text{Hydrolysis}} \underset{\text{Aluminimum hydroxide}}{2Al(OH)_3} + \underset{\text{Silica hydroxide}}{2Si(OH)_4} + Ca^{2+} \tag{6.5}$$

$$\underset{\text{From hydrolysis of minerals}}{Ca^{2+}} + CO_3^{2-} \rightarrow \underset{\text{Secondary calcium carbonate}}{CaCO_3 \downarrow} \tag{6.6}$$

Mainly, soluble calcium added through an exogenous source and or mobilized by dissolving calcite is used to replace Na^+ from the exchange complex and reclaim alkali soils (Eq. 6.1). Based on their nature, amendments have been classified into the following three categories.

6.4.1 Chemical Amendments

6.4.1.1 Ca-Supplying Amendments

Amendments like calcium chloride ($CaCl_2.2H_2O$), calcium nitrate ($Ca(NO_3)_2$, and calcium sulphate dihydrate ($CaSO_4.2H_2O$) commonly known as gypsum, directly supply soluble Ca^{2+} to replace exchangeable-Na^+ and thus lower ESP and pH of alkali soils. **Calcium chloride** is a white coloured crystalline inorganic salt highly soluble in water (745 g L^{-1} at 20 °C). Calcium chloride under natural conditions occurs as hygroscopic antarcticite mineral [($CaCl_2.6H_2O$); Torii and Ossaka 1965)] in highly saline soils. This is very unstable and cannot be mined for commercial use.

The commercially available $CaCl_2$ is manufactured from naturally occurring underground brine through Solvay process using high purity limestone. Salt concentration of underground brine is usually more than 100,000 mg L^{-1}. It is further concentrated and purified for the production of soda ash (Na_2CO_3) with $CaCl_2$ as by-product (Eq. 6.7). It is also produced from hydrochloric acid and limestone (Eq. 6.8) or quick lime, burnt lime (Eq. 6.9).

$$\underset{\text{Lime stone}}{CaCO_3} + \underset{\text{Salt brine}}{2NaCl} \rightarrow \underset{\text{Soda ash}}{Na_2CO_3} + \underset{\text{Calcium chloride}}{CaCl_2} \tag{6.7}$$

$$\underset{\text{Lime stone}}{CaCO_3} + \underset{\text{Hydrochloric acid}}{2HCl} \rightarrow \underset{\text{Calcium chloride}}{CaCl_2} + \underset{\text{Carbon-di-oxide}}{CO_2} + H_2O \tag{6.8}$$

$$\underset{\text{Burnt lime}}{CaO} + \underset{\text{Hydrochloric acid}}{2HCl} \rightarrow \underset{\text{Calcium chloride}}{CaCl_2} + H_2O \tag{6.9}$$

It is available as dry salt in crystal form, as anhydrous $CaCl_2$ flakes containing 77–80% $CaCl_2$, anhydrous granules / prills containing 94–96% $CaCl_2$ and as liquid solution with concentration ranging from 28 to 42%. Dry $CaCl_2$ is also used for melting ice on roads, in refrigeration brine, for dust control in mining operations and as anti-frosting agent for concrete.

Singh and Nijhawan (1932), Puri (1932, 1934, 1949) and Talati (1947) compared efficiency of calcium chloride with gypsum under field conditions and found it superior to gypsum. This was mainly due to its high solubility. Shainberg et al. (1982) observed faster improvement in alkali soils on combined application of gypsum and $CaCl_2$. However, as compared to other amendments, calcium chloride is costly and unless it is available as industrial waste or by-product, its use for reclamation of alkali soils is not economical. **Calcium nitrate** [$Ca(NO_3)_2$] is a good amendment and helps in improving chemical and physical properties of alkali Vertisols (Cairns 1971, 1980). It also supplies N and Ca as nutrients. But considering the cost, it is mostly used as a fertilizer rather than Ca-supplying amendment for alkali soils.

Use of **gypsum** for reclamation of alkali soils was suggested by Leather as early as 1906. He calculated gypsum requirement on the basis of soluble carbonates needed to be neutralized. The concept of exchangeable-cations and role of exchangeable-sodium in alkali soils had not developed till that time. Kelley and Arany (1928) studied its effect on chemical properties of alkali soils in comparison to sulphur, iron sulphate and alum and found it better than others. Since, there was no support of the government to supply and to subsidize its cost, use of gypsum for reclamation of alkali soils remained confined to government farms till long-times. Because of its easy availability, cost effectiveness, unproblematic transportation and safe handling in field, mineral gypsum or mined-gypsum is now widely used for reclamation of alkali soils. In column studies, Silveira et al. (2008) observed improvement in physical and chemical characteristics of alluvial saline-sodic and sodic soil of Northeast Brazil, when leached with gypsum-saturated water. As its solubility in water is very low (2.60 g L^{-1} at 25 °C), it can be easily stored in open, near and in fields, without any serious damage from rains. While acting as a soil

Table 6.13 Specifications for agricultural grade gypsum (IS 6046: 1982b, 2003)

Parameters	Limits
Calcium sulphate content ($CaSO_4.2H_2O$)	Shall not be less than 70%.
Fineness	All material shall pass through 2 mm sieve but at least 50% of it should pass through 0.25 mm (60 mesh) sieve.
Sodium content	Shall not be more than 0.75%.

Source: Bureau of Indian Standards (1982b)

conditioner and ameliorant for alkali soils, it also supplies nutrients like Ca and S for plant growth. Since it is a mined material and can be adulterated with other low-cost materials like sand and soil, Bureau of Indian Standards, New Delhi, India (1982b) has fixed the following specifications for agricultural grade gypsum (Table 6.13).

6.4.1.2 Acids

Acids, directly react with soluble CO_3^{2-} and HCO_3^- reducing residual alkalinity of soil solution (Eqs. 6.10 and 6.11) and dissolve native insoluble calcite to provide soluble-Ca^{2+} in situ (Eq. 6.12) required for replacing exchangeable-Na^+ to lower ESP (Eq. 6.13). In the absence of enough $CaCO_3$, the hydrogen ions of acids also directly replace exchangeable-Na^+ leading to formation of degraded alkali soils (Eq. 6.14).

$$Na_2CO_3 + H_2SO_4 \rightarrow Na_2SO_4 + CO_2 + H_2O \quad (6.10)$$

$$2NaHCO_3 + H_2SO_4 \rightarrow Na_2SO_4 + 2CO_2 + 2H_2O \quad (6.11)$$

$$CaCO_3 + H_2SO_4 \rightarrow CaSO_4 + CO_2 + H_2O \quad (6.12)$$

$$Na^+\text{-soil} + CaSO_4 \rightarrow Ca^{2+}\text{-soil} + Na_2SO_4 \downarrow \quad (6.13)$$

$$H_2SO_4 + Na^+\text{-soil} \rightarrow Na^+, H^+\text{-soil} + Na_2SO_4 \downarrow \quad (6.14)$$

In alkali soils of Kamma series (Khanna, Punjab, India), Kanwar and Bhumbla (1960) compared the efficiency of commercial grade sulphuric acid, nitric acid and hydrochloric acid against other amendments and found H_2SO_4 was better than others. Yadav (1973) compared the effect of gypsum and sulphuric acid applied at 80% of the laboratory estimated GR and in chemically equivalent quantities on crop yields in a highly sodic soil. pH and ESP of surface soil of the experimental field varied between 9.1 to 9.8 and 41 to 60, respectively. Yield of rice and wheat over three-years of study (Table 6.14) were higher in sulphuric acid than in gypsum treated plots.

Mace et al. (1999) compared efficiency of H_2SO_4 and gypsum on equivalent basis on calcareous sodic soils and clays in the laboratory and found that application of H_2SO_4 generally resulted in lower sodium adsorption ratio, more soluble-Ca^{2+} and

Table 6.14 Effect of gypsum and equivalent quantities of sulphuric acid on crop yields, t ha^{-1}, in a highly alkali soil

Treatments	First year		Second year		Third year		Mean	
	Rice	Wheat	Rice	Wheat	Rice	Wheat	Rice	Wheat
Control	1.51	0.72	2.12	1.71	3.56	1.46	2.40	1.30
Gypsum	3.67	1.92	4.36	2.61	5.13	2.74	4.39	2.42
Sulphuric acid	4.56	2.56	4.68	3.10	5.53	3.05	4.92	2.90

Source: Yadav (1973)

Mg^{2+}, lower pH, and greater EC. Higher effectiveness of H_2SO_4 may also be because calcium sulphate formed in situ is more effective in replacing the adsorbed sodium. Prather et al. (1978) reported that H_2SO_4 was superior to gypsum when both were applied @ 80% GR of the soil. They further suggested that combining either $CaCl_2$ or H_2SO_4 with $CaSO_4.2H_2O$ as an amendment can appreciably shorten the time of reclamation and improve water efficiency as compared to $CaSO_4.2H_2O$ alone under certain soil conditions. Milap Chand et al. (1977) while comparing eight chemical amendments for reclamation of a highly alkali soil at Karnal, India, found gypsum superior to sulphuric acid.

Concentration of H_2SO_4 to be added to soil for reclamation may vary from 1 to 6%. The amount of acid required is calculated from the amount of residual alkalinity $[(H_2CO_3^- + CO_3^{2-}) - (Ca^{2+} + Mg^{2+})]$ of saturated soil paste extract and the amount of exchangeable-sodium to be removed from the soil (Pankova et al. 2009). The rates may vary widely depending on the soil properties. Soda-saline Solonetz soils in Armenia (pH 9–11, ESP > 20) required 60–80 t of sulphuric acid ha^{-1} to neutralize alkalinity of top 1 m layer (Lyubimova et al. 2009). Sulphuric acid reacts directly with soil-lime as it has not to go through the oxidation process. Hence, its efficiency is more than pyrites and elemental sulphur.

Sulphuric acid is being increasingly used for improving calcareous alkali soils in many parts of the United States, because there its cost as compared to that of gypsum is not prohibitive and its use is economical as larger and quicker returns from land, in the form of crop yields, pay for the higher initial cost. Similarly, in USSR, large-scale soil reclamation has been done in the Ararat Valley, in the Armenian Republic by application of 1% sulphuric acid along with heavy leaching (Petrosian 1977). However, due to high cost, corrosive nature and hazards in handling under field conditions, use of acids have not found acceptability with the Indian farmers.

6.4.1.3 Acid Formers

(a) **Pyrites**

Pyrites (Iron di-sulphide, FeS_2), a naturally occurring sedimentary mineral, furnishes soluble Ca^{2+} indirectly by first oxidizing its sulphur to an acid, which in turn reacts with soil-lime to furnish soluble calcium (Eqs. 6.15, 6.16, and 6.17).

$$2FeS_2 + 2H_2O + 7O_2 \rightarrow 2FeSO_4 + 2H_2SO_4 \quad (6.15)$$

$$CaCO_3 + H_2SO_4 \rightarrow CaSO_4 + CO_2 + H_2O \quad (6.16)$$

$$2Na^+\text{-soil} + CaSO_4 \rightarrow Ca^{2+}\text{-soil} + Na_2SO_4 \downarrow \quad (6.17)$$

Oxidation of pyrites (Eq. 6.15) depends both on moisture content and oxygen availability in soil. In waterlogged soils, it is limited due to poor oxygen availability while in dry soils it is inhibited due to low availability of moisture. Hence, for better results pyrites should be applied in soils with enough moisture (at *vattar* conditions) and high oxygen supply to encourage oxidation of sulphur. To increase its efficiency and to leach the reaction products, a cycle of wetting and drying is a must. Oxidation period of 7 days followed by submergence (5 cm depth of water) for next 7 days resulted in higher reclamation efficiency of pyrites (Sharma and Gupta 1986). Bureau of Indian Standards (1996) New Delhi, India, based on total S-content, has fixed the following specifications for agricultural grade pyrites (Table 6.15). It needs further improvement by including the minimum soluble-S content of the material.

Chemical oxidation of pyrites starts as soon as the material is mined and exposed to air. The reaction, though slow is wasteful as some of the S may escape to atmosphere as sulphur-di-oxide (Eq. 6.18) and is not available for acid production. To minimize this wastage, it is important that its oxidation is encouraged under moist conditions where SO_2 can be directly converted into H_2SO_4 and used for reclamation.

$$\underset{\text{Pyrites}}{FeS_2} + \underset{\text{Atmospheric oxygen}}{3O_2} \xrightarrow{\text{Chemical oxidation}} \underset{\text{Ferrous sulphate}}{FeSO_4} + \underset{\text{Sulphur di-oxide}}{SO_2 \uparrow} \quad (6.18)$$

The major sulphur oxidation, referred as "biological oxidation" is mediated though the bacteria *Thiobacillus ferrooxidans* which requires a warm, well aerated moist soil and low pH of 2–3 for efficient working. *Thiobacillus ferrooxidans* also known as *Acidithiobacillus ferrooxidans* are colourless rod-shaped bacteria and derive their energy from oxidation of ferrous iron to ferric iron and oxidize sulphur compounds to sulphuric acid. These grow on reduced forms of sulphur (S^0, S^{2-}, $S_2O_3^{2-}$), reduced form of metals (Fe^{2+}, Sn^{2+}, Cu^{2+}) and are extensively used for

Table 6.15 Indian standard specifications for agricultural grade pyrites (IS 14403: 1996)

Parameters	Limits
Sulphur content	Shall not be less than 16%
Fineness	90% of the material shall pass through 5 mm sieve and at least 50% of it should pass through 3 mm sieve
Iron content	Shall not be more than 25% by mass
Aluminium content	Shall not be more than 10% by mass

Source: Bureau of Indian Standards (1996)

Table 6.16 Influence of initial pH of the medium on yield of iron with the use of *Thiobacillus ferrooxidans* bacteria at a temperature of 37 °C

Initial pH of the medium	Conc. of Fe (III) in the medium, g dm^{-3}
1.1	0.26
1.7	0.65
2.0–2.4	0.78
2.4–2.8	0.23

Source: Nowaczyk et al. (1998)

bioleaching of metal ions from low grade ores. Nowaczyk et al. (1998) observed that at very low pH of 1.1, it is the chemical oxidation while at pH above 1.7 it is the biological process which plays a major role in oxidation of sulphur. They observed that maximum dissolution of iron from FeS_2 was at pH between 2.0 and 2.4 (Table 6.16). Another species *Acidithiobacillus thiooxidans*, a gram-negative rod-shaped bacterium, also oxidizes S^0 into H_2SO_4. It is an obligate acidophile which works at an optimal pH of less than 4.0. It is an aerobe and chemolithotroph. A chemolithotroph is able to use inorganic reduced compounds as a source of energy through the process of oxidation and ATP synthesis. More efficient S-oxidizing bacterias naturally occurring in sulphur springs, sulphur dumping sites and active in acid sulphate soils should be isolated, identified, and cultured to develop inoculums for speedy oxidation of sulphur in pyrites under field conditions.

Since in alkali soils, pH is always above this critical value, oxidation of all the S present in FeS_2 is never complete. Further, when pyrites are added to alkali soils, the acid already contained in it (formed due to chemical oxidation) gets neutralized by soluble CO_3^{2-}, HCO_3^- and calcite of soil. Due to this and high alkalinity of soil, pH in the vicinity of pyrites granule increases and drastically slows down its biological oxidation. As a result of this, the entire S contained in pyrites is not oxidized and thus its efficiency when applied on "total sulphur" equivalent basis remains much below than that of gypsum. Verma and Abrol (1980a, b) found that efficiency of pyrites in terms of crop yields and improvement of alkali soils was much less than equivalent amount of gypsum (Table 6.17).

To have better results from pyrites, following guidelines should be adopted:

(i) Use pyrites containing 4–6% soluble-S and of pH less than 3, because efficiency of pyrites depends upon its soluble-S content as well as on its total-S content.

(ii) Encourage maximum oxidation of pyrites before applying it to alkali fields. This can be achieved by storing the freshly mined pyrites for a period of 10–20 days in a well-aerated place under moist conditions, approximately at 10% moisture level.

(iii) During transport and storage, pyrites should be well protected from rains otherwise soluble-S (H_2SO_4 formed) will be washed away leading to lower efficiency of the rain-washed material. The rain-washed pyrites is almost inert and have poor efficiency as soil amendment.

Table 6.17 Effect of gypsum and equivalent quantities of pyrites on crop yields and soil properties of a highly sodic soil

Treatments	Crop yield, t ha^{-1}		Soil Properties		
	Rice	Wheat	Infiltration rate, mm day^{-1}	ESP	
				0–15 cm	15–30 cm
Control	3.85	0.19	3.34	76.5	92.4
Gypsum, t ha^{-1}					
7.1 (25% GR)	6.71	1.46	6.82	33.4	75.1
14.2 (50% GR)	6.85	3.14	8.58	32.4	79.2
21.3 (75% GR)	7.43	3.60	12.25	19.2	59.5
28.4 (100% GR)	7.24	4.22	12.42	13.6	56.5
Pyrites, t ha^{-1}					
3.6 (25% GR)	5.71	0.15	3.30	64.1	90.2
7.2 (50% GR)	6.04	0.54	4.05	52.3	86.4
10.8 (75% GR)	6.71	1.35	5.62	44.1	80.2
14.4 (100% GR)	6.91	1.39	5.65	38.8	80.3

Source: Verma and Abrol (1980a)

(iv) After application of pyrites or elemental-S or by-product-S, in the field, instead of continuous ponding of water, cycles of alternate wetting and drying should be adopted to help increase their oxidation and thus efficiency. Moist but well aerated soil conditions (40–60% water filled pore space, WFPS) to promote oxidation of elemental-S (Jaggi et al. 2005) and saturated soil conditions to promote leaching of the reaction products, increases its efficiency.

(v) Oxidation of S is more at higher temperature (> 25 °C) and is minimal at temperature < 5 °C (Zhihui et al. 2008). So, when pyrites is the amendment of choice then it is better to start reclamation in summer season with *Kharif* crops rather than in winter season with *Rabi* crops.

But despite all this, many studies (Table 6.18) have shown that its efficiency is much less as compared to gypsum at the recommended doses of application. These conflicting reports are due to comparison of pyrites based on its total-S content, oxidation of which is never complete in high pH alkali soils.

(b) Elemental Sulphur

Elemental sulphur is mined from ores in the form of "molten sulphur" and used for making H_2SO_4 which is a basic raw material for rubber, plastic, insecticides and fertilizer industries. Sulphur is also used as such as fungicides (Sulphur dust). Sulphur in the form of bright yellow powder known as "Flower of sulphur" is also obtained from naturally occurring volcanic brimstone deposits. Though it looks like powder, it consists of fine crystals having the shape of flowers. But now-a-days almost all commercially available S is obtained as by-product-S from petroleum industry. A small amount is also produced as a by-product from ferrous and non-ferrous metal smelting units.

Table 6.18 Effect of gypsum and pyrites on the yield of rice in alkali soils

Type of soil and initial pH	Crops	Grain yield, t ha^{-1}, at different levels (% GR) of amendments										Source
		0		25		50		75		100		
		G	P	G	P	G	P	G	P	G	P	
Alfisol, pH_2 10.5	Rice Wheat	3.86 0.02	3.86 0.02	6.71 1.46	5.71 0.15	6.81 3.15	6.09 0.54	7.44 3.60	6.71 1.35	7.24 4.22	6.91 1.35	Abrol and Verma (1978)
Alfisol, pH_2 9.2	Rice Barley	1.73 2.62	1.73 2.62	–	–	2.77 3.67	0.54 3.64	–	–	–	–	Chauhan (1978)
Alfisol, farmers field pH_2 varying from 9.0 to 10.5	Rice Wheat	2.93 1.50	2.93 1.50	3.23 1.18	3.49 1.18	3.57 1.74	3.87 1.27	3.13 1.58	4.06 1.60	4.09 2.33	4.87 1.86	Bhatt et al. (1978)
Alfisol, pH_2 10.2	Rice Wheat	2,61 2.05	2.61 2.05	–	6.65[a] 3.72	6.87 4.80	–	–	7.59[b] 4.84	–	7.66 5.00	Singh et al. (1981)
Vertisol, pH_2 8.5	Rice Wheat	0.14 0.50	0.14 0.50	0.97 1.00	0.84 0.88	1.77 1.67	1.60 1.51	2.50 2.40	2.18 3.22	–	–	Sharma and Gupta (1986)
Alfisol, pH_2 10.2	Rice	1.75	1.75	2.93	2.09	3.06	2.37	–	–	3.43	2.60	Chhabra et al. (1989)

G Gypsum, *P* Pyrites

[a]33% GR

[b]66% GR Similarly, iron sulphate heptahydrate ($FeSO_4.7H_2O$) on hydrolysis produces H_2SO_4 (Eq. 6.22) which helps in dissolving native $CaCO_3$ which in turn is used to replace exchangeable-Na^+

Conversion of mineral sulphur to H_2SO_4 (Eq. 6.19), which takes place through biological oxidation, is very low and slow in alkali soils. Due to this reason, the relative efficiency of mineral-S and by-product-S is also not high in alkali soils.

$$\underset{\text{Elemental sulphur}}{2S} + 3O_2 + 2H_2O \xrightarrow{\text{Biological oxidation}} \underset{\text{Sulphuric acid}}{2H_2SO_4} \tag{6.19}$$

McGeorge and Greene (1935) reported that even increasing the fineness of coarse natural sulphur from 16–70 mesh to 200 mesh and inoculation with microorganisms did not have any effect on its efficiency.

Kelley (1937) observed that S when applied together with alfalfa as green manure (GM) had a slow but positive effect on reclamation of black alkali soils. It was postulated that CO_2 and organic acids produced by the decomposition of GM together with increase in microbial population, favoured biological oxidation of sulphur. When applied along with FYM, it proved to be an effective amendment for increasing yield of sugarcane (Basu and Tagare 1943; Talati 1947) and for cotton (Gidnavar et al. 1972) in black alkali soils.

(c) **Aluminium sulphate and Iron sulphate**

Aluminium sulphate [$(Al_2(SO_4)_3.18H_2O$] is commonly used as a coagulating / flocculating agent in purifying turbid waters, treatment of sewage effluents and in paper industry. When added to soil, it hydrolysis into aluminium hydroxide $Al(OH)_3$ and sulphuric acid (Eq. 6.20). The acid reduces pH of the soil and helps in dissolving native $CaCO_3$. Aluminium ions (Al^{3+}) help in better aggregation of soil and thereby improve the infiltration rate (Table 6.20).

$$\underset{\text{Aluminium suphate}}{Al_2(SO_4)_3.18H_2O} \xrightarrow{\text{Hydrolysis}} \underset{\text{Aluminium hydroxide}}{2Al(OH)_3\downarrow} + \underset{\text{Sulphuric acid}}{3H_2SO_4} + 12H_2O \tag{6.20}$$

The anhydrous form of aluminium sulphate occurs naturally as a rare mineral millosevichite [$Al_2(SO_4)_3$] (Anthony et al. 2003), found in volcanic environments and on burning coal-mining waste dumps. Commercially, aluminium sulphate is manufactured by reaction of $Al(OH)_3$ with sulphuric acid (Eq. 6.21). It forms a number of different hydrates, of which hexahydrate [$Al_2(SO_4)_3.6H_2O$], hexadecahydrate [$Al_2(SO_4)_3.16H_2O$] and octadecahydrate [$Al_2(SO_4)_3.18H_2O$] are the most common.

$$\underset{\text{Aluminium hydroxide}}{2Al(OH)_3} + \underset{\text{Sulphuric acid}}{3H_2SO_4} + 12H_2O \rightarrow \underset{\text{Octadecahydrate aluminium sulphate}}{Al_2(SO_4)_3.18H_2O} \tag{6.21}$$

$$\underset{\text{Ferrous sulphate}}{FeSO_4.7H_2O} \xrightarrow{\text{Hydrolysis}} \underset{\text{Ferrous hydroxide}}{Fe(OH)_2\downarrow} + \underset{\text{Sulphuric acid}}{H_2SO_4} + 5H_2O \tag{6.22}$$

Ferrous sulphate heptahydrate, commonly known as copperas, is a green, water soluble, acidic salt, produced as a by-product during the manufacture of TiO_2 from ilmenite, also known as manaccanite, a titanium-iron oxide mineral with the idealized formula of $FeTiO_3$. It is also produced from natural mined pyrites.

Table 6.19 Equivalent amount of various amendments for supplying Ca in terms of pure gypsum

Amendments	Physical appearance	Amount equivalent to 100% gypsum[b]
Gypsum ($CaSO_4.2H_2O$)	White powder	1.00
Agricultural grade gypsum (70% purity)	White mineral, powder	1.43
Calcium chloride ($CaCl_2.2H_2O$)	White crystalline salt, hygroscopic, byproduct	0.85
Calcium nitrate [$Ca(NO_3)_2.2H_2O$]	White to light grey, granular, hygroscopic	1.06
Sulphitation press mud (lime-Sulphur; 9% Ca, 24% S)	Black to light brown, byproduct	0.78
Sulphuric acid (H_2SO_4)	Corrosive liquid	0.61
Iron sulphate ($FeSO_4.7H_2O$)	Blue green salt, byproduct	1.62
Ferric sulphate [$Fe_2(SO_4)_3.9H_2O$]	Yellow-brown salt, byproduct	1.09
Aluminium sulphate [$Al_2(SO_4)_3.18H_2O$]	Corrosive granules,	1.29
Sulphur (S)[a]	Yellow powder, byproduct	0.19
Pyrites (FeS_2, 30% S)	Yellow black mineral	0.63

[a]Oxidation of 100% S is assumed. In practice this does not happen and thus its effectiveness under field conditions is much lower than that of other amendments
[b]The quantities are based on 100% pure materials. If not, then necessary corrections must be made. As for agricultural grade gypsum which is of 70% purity, the equivalent quantity to be applied will be (100 x1) ÷ 70 i.e. 1.43 tonnes

Chemical amendments cost money. The benefit of any amendment should be tested in field trials for its effectiveness, safety in use, and cost-benefit ratio. The theoretical amounts of various amendments to supply Ca^{2+} equivalent to 1 tonne of gypsum are given in Table 6.19.

Exchange of cation in soil is governed by the type of cation (its valency, size and degree of hydration), its concentration, nature of anion associated with the cation, and nature of clay particles. H^+ has the same valency of one as that of Na^+ but is smaller in size [empirical radii of H^+ is 25 picometers (pm) or 0.25 A while that of Na^+ is 180 or 1.80 A; Cotton and Wilkinson 1988] and non-hydrated so it has greater replacing power and is preferred over Na^+ in the exchange complex. Thus H^+ of H_2SO_4 formed during hydrolysis of $Al_2(SO_4)_3.18H_2O$ and $FeSO_4.7H_2O$ or by oxidation of sulphur in pyrites or directly supplied by H_2SO_4 as such, may also directly replace Na^+ from the exchange complex and lower soil ESP.

6.4.1.4 Chemical Amendments and Soil Physical Properties

Effect of chemical amendments on improving soil physical properties should also be considered along with their effect on soil chemical properties. Verma et al. (1985) observed that though ESP decrease was similar in H_2SO_4 and gypsum treatments (Table 6.20), saturated hydraulic conductivity of soil was less and water dispersible

Table 6.20 Effect of different cations associated with the amendments (applied at the rate of 100% GR) on physico-chemical properties of an alkali soil

Amendments	Dominating cation	pH_2	EC, dS m^{-1}	ESP	Saturated hydraulic conductivity, mm h^{-1}	Water dispersible clay, %	Dispersion ratio
Control	Na^+	8.8	9.80	65	0.06	37.2	0.41
Gypsum $CaSO_4.2H_2O$	Ca^{2+}	7.9	0.72	14	4.77	8.0	0.09
Pyrites, Ferrous disulphide, FeS_2	Fe^{2+}	8.0	0.31	20	1.64	32.4	0.36
Sulphuric acid H_2SO_4	H^+	7.5	0.18	14	2.98	30.4	0.54
Aluminium sulphate $Al_2(SO_4)_318H_2O$	Al^{3+}	7.6	0.27	8	4.49	8.6	0.09
Ferrous sulphate $FeSO_4.7H_2O$	Fe^{2+}	7.9	0.85	21	1.59	33.7	0.37
LSD at P = 0.5	–	0.35	0.25	2.9	0.97	3.5	–

Source: Adopted from Verma et al. (1985)

clay greater in H_2SO_4 treatments. Similarly, ESP drop and improvement in physical properties was greater when $Al_2(SO_4)_3.18H_2O$ was applied as amendment. This seems to be due to Ca^{2+} and Al^{3+} of gypsum and $Al_2(SO_4)_3$ respectively, which are more effective flocculants than H^+ of H_2SO_4 and Fe^{2+} of pyrites or ferrous sulphate. Furthermore, $CaSO_4.2H_2O$ solubilizes slowly, as a result of which, a major part of this is not immobilized by soluble $NaHCO_3$ and Na_2CO_3 (the major soluble salts present in alkali soils) but is effectively used for replacing exchangeable-Na^+ and maintaining threshold electrolyte concentration required for flocculation of dispersed inorganic colloids.

6.4.2 *Organic Amendments*

Alkali soils are generally low in organic matter. Addition of crop residues and other organic materials in soils are beneficial as these help to improve and maintain soil structure, supply needed plant nutrients, prevent soil erosion and hasten the rate of reclamation. Most commonly used organic amendments are materials like rice straw, rice husk, poultry droppings, groundnut husk, sunflower hulls, farm yard manure (FYM), compost, green-manure, tree leaves, sawdust and molasses etc. Organic amendments, on their decomposition, produce high partial pressure of carbon dioxide and organic acids, which help to increase electrolyte concentration, lower soil pH and redox potential (Swarup 1988). These processes in turn increase the solubility of calcite and thereby lower ESP (Puttaswamygowda and Pratt 1973). To achieve maximum benefits from organic amendments, high moisture levels are to be maintained during the course of their decomposition. Singh (1974) observed that when barley straw and *Sesbania* were decomposed under aerobic conditions (i.e. at moisture level near field capacity), their efficiency in terms of reduction in ESP and improvement in soil physical properties (Table 6.21) was less as compared to when

Table 6.21 Effect of C:N ratio of organic matter and moisture condition on improvement in calcareous silty clay alkali alluvial soil

Treatments	pHs	ESP	Modulus of rupture, bars	Hydraulic conductivity, cm h^{-1}	Na^+ in the leachate, me L^{-1}
Barley straw aerated	9.1	81.5	12.9	0.03	16.6
Barley straw saturated	8.4	56.1	11.3	1.72	30.2
Sesbania aerated	8.8	68.5	11.8	0.04	26.3
Sesbania saturated	8.3	47.2	7.5	1.29	43.0
Original soil	9.5	95.0	NA	NA	NA

Source: Singh (1974)
[a]Added at the rate of 2% by weight

those were decomposed under anaerobic conditions (i.e. at moisture level near saturation). Higher efficiency under anaerobic conditions was due to trapping of mineralized CO_2 and its conversion to carbonic acid (H_2CO_3) which in turn increased the solubility of native $CaCO_3$. Further, *Sesbania* due to its narrow C:N ratio decomposed faster as compared to barley straw and was more efficient in lowering ESP.

Due to their coarse texture and slow decomposition, these materials do not allow the pores to be clogged and physically keep the soil porous by maintaining channels and voids which improve water penetration and leaching of salts and reaction products. Thus, these also act as physical amendments. Khosla (1976) observed that incorporation of rice husk @ 10, 20, 30, 40 and 50 t ha^{-1} increased the infiltration rate of an alkali soil (ESP 74) from 2.25 (in control) to 2.55, 4.81, 4.94, 5.64 and 6.49 cm day^{-1}, respectively.

Because of their synergetic effects, organic materials together with inorganic amendments are more cost-effective, hasten the reclamation process, increase yield and therefore their conjunctive use is beneficial (Talati 1947; Dargan et al. 1976; Dargan 1979; Chaudhary and Bajwa 1979). Mendiratta et al. (1972) observed that rate of gypsum dissolution was enhanced by incorporating FYM and green-manure. Sharma (1988) obtained better reduction in ESP when FYM was incorporated with pyrites. Yield of berseem, sugarcane and rice in alkali alluvial soils of the Indo-Gangetic plains increased significantly by incorporating FYM with gypsum in comparison to their individual application (Dargan 1979). Swarup and Singh (1993) observed that application of FYM @ 20 t ha^{-1} alone was inferior to gypsum. But when combined with gypsum, it gave higher yields than gypsum alone and hastened the reclamation of alkali soils (Table 6.22). FYM has a complementary effect on increasing the efficiency of gypsum and reducing ESP of soil but is less efficient than gypsum when applied alone. Similarly, efficiency of green manuring, wheat straw and crop cultivation in improving saturated hydraulic conductivity of a

Table 6.22 Effect of gypsum levels and FYM[a] on yield of rice and wheat in an alkali alluvial soil

Application rates		Grain yield, t ha^{-1}						
		Rice			Wheat			
Gypsum, % GR	FYM, t ha^{-1}	1st year	2nd year	3rd year	1st year	2nd year	3rd year	ESP after 3 years
Nil	Nil	2.98	4.55	5.20	0.20	1.00	1.20	55
25	Nil	5.10	5.23	5.30	1.67	2.30	2.30	48
50	Nil	5.44	5.46	5.30	1.99	2.30	2.40	42
Nil	20	4.05	5.20	5.30	1.42	2.00	2.20	56
25	20	5.78	5.76	5.80	2.14	2.80	2.80	38
50	20	6.13	6.01	5.90	2.36	2.80	2.90	35
LSD at P = 0.05		0.33	0.41	0.40	0.35	0.36	0.34	–

Initial pH_2 = 10.4, ESP = 89, Rice, cv. Jaya, Wheat, cv. HD 2009
Source: Swarup and Singh (1993)
[a]Gypsum and FYM were applied at the start of the experiment

Table 6.23 Effect of gypsum, green manuring, wheat straw and crop cultivation on the field saturated hydraulic conductivity of a fine loamy alkali soil[a] in Pakistan

Treatments	Saturated hydraulic conductivity (Ks,10^{-7} m s^{-1}) of different soil depths			
	Without gypsum			
	0–20 cm	20–40 cm	40–60 cm	60–80 cm
Alfalfa (*Medicago sativa*)	2.4ab[b]	3.8a	2.0a	3.4a
Wheat straw @ 7.5 t ha^{-1}	1.8b	1.4b	1.1a	1.1b
Sesbania (GM)-wheat-sesbania (GM)	3.4a	1.9b	1.9a	1.7b
Fallow	1.2b	1.1b	1.6a	2.6b
	With gypsum @ 25 t ha^{-1}			
Alfalfa	6.5a	3,9a	4.4a	4.2b
Wheat straw @ 7.5 t ha^{-1}	3.5b	2.1b	1.8b	2.9b
Sesbania (GM)-wheat-sesbania (GM)	7.9a	2.0b	1.8b	2.1b
Fallow	2.9b	1.2b	1.2b	1.5b

Source: Ilyas et al. (1993)
[a]pHs 8.8, ECe 5.6 dS m^{-1}, SAR 49
[b]Means followed by the same letter within a column are not statistically different (P = 0.05)

high SAR-saline soil was more in conjugation with gypsum (chemical amendment) as compared to when practiced alone (Ilyas et al. 1993, Table 6.23).

Use of organic materials as amendments is economical when these are available locally with the farmer and are free of cost. But when these are to be purchased then these are not economical than gypsum alone. Also, to be effective alone, relatively large quantities (20 to 50 t ha^{-1}) of organic amendments have to be used. If the C:N ratio of these materials is very wide, as is the case with sawdust and rice husk, then they decompose slowly and are less effective as compared to sesbania which due to its narrow C:N ratio decomposes faster. Under these conditions, deficiency of N may also occur and needs to be taken care of. In areas infested with termites (*Isoptera*), application of large amounts of organic matter may intensify damage to the upland crops. Under certain situations salinity-effects, especially with cow-dung and piggery slurry, may be a limiting factor for their continuous use.

As an alternative to FYM, other materials mostly weeds, such as ipomoea (*Ipomea purpurea*, *I. indica*) collected from marshy wastelands and *Satyanashi,* Mexican poppy (*Argemone mexicana*) collected from adjoining wastelands, have also been used at Bhanthra Farm near Lucknow, Uttar Pradesh and at Kamma Farm near Khanna in Punjab, India (Kanwar et al. 1965). Their efficiency was low as compared to sesbania. Being weeds, these can also become a problem for the farmers. Molasses from the sugarcane industry and spent wash from the distillery / alcohol industry are another waste materials which can be used for reclamation of alkali soils (Dhar and Mukerjee 1938; Escolar 1966). But these materials contain high amounts of salts and thus can increase salinity of soil.

6.4.3 *Industrial by-Products as Amendments*

Sources of mineral gypsum and pyrites are limited, so industrial by-products which will be available in abundance for long time to come, are the viable alternative to reclaim and fertilize alkali soils. As these materials are cheap and locally available, their use should be encouraged. Industrial by-products like phosphogypsum, press mud, molasses, acid wash and effluents from milk plants may be used for reclamation purposes as these provide soluble-Ca^{2+} directly, or indirectly by dissolving soil-lime. However, care should be taken not to introduce toxic elements like F, which may be present in large amounts in by-products like phosphogypsum (Chhabra et al. 1980a, b) and Pb, Cd and Ni present in fly ash. Potential uses of some industrial by-products suitable as amendment for reclamation of alkali soils are discussed below:

6.4.3.1 Phosphogypsum

Phosphogypsum is a by-product of phosphate industry where phosphoric acid (H_3PO_4) is produced, through wet-acid process, from mineral rock phosphate [RP, $Ca_3(PO_4)_2.CaX_2$] and sulphuric acid (H_2SO_4) (Eq. 6.23). X in CaX represents F, Cl, OH or CO_3 making fluorapatite [$(3Ca_3(PO_4)_2.CaF_2)$], chlorapatite [$(3Ca_3(PO_4)_2.CaCl_2)$], hydroxyapatite [$(3Ca_3(PO_4)_2.Ca(OH)_2$], and carboxyapatite [$(3Ca_3(PO_4)_2.CaCO_3$], respectively.

$$\underset{\text{Rock phosphate}}{3Ca_3(PO_4)_2.CaF_2} + \underset{\text{Sulphuric acid}}{10H_2SO_4} + \underset{\text{Water}}{10H_2O} \rightarrow \underset{\text{Phosphoric acid}}{6H_3PO_4} + \underset{\text{gypsum}}{10CaSO_4.2H_2O\downarrow} + \underset{\text{Hydrogen fluoride}}{2HF} \quad (6.23)$$

Phosphoric acid produced is used as a chemical and for production of di-ammonium phosphate fertilizer. Insoluble gypsum gets settled down and is separated through filtration. During this process some amount of phosphoric acid (H_3PO_4) also get separated along with gypsum and thus the by-product is called phosphogypsum. However, all the fluoride also settles down as CaF_2 (Eq. 6.24) along with phosphogypsum, affecting its quality.

$$\underset{\text{Rock phosphate}}{Ca_3(PO_4)_2} + \underset{\text{Hydrogen fluoride}}{6HF} \rightarrow \underset{\text{Phosphoric acid}}{2H_3PO_4} + \underset{\text{Calcium fluoride}}{3CaF_2\downarrow} \quad (6.24)$$

Phosphogypsum is a grey-coloured, damp, fine grained powder having grain size between 0.5 mm and 1.00 mm (20 mesh), the majority of particles (50–75%) are finer than 0.75 mm (200 mesh). It contains small amounts of silica, usually as quartz, untreated rock phosphate, heavy metals like As, Cd, Cr, Hg, and F as impurities; concentration of which depends upon the composition of rock phosphate. It also

contains radioactive Radium-226 and Uranium-238 as naturally occurring radioactive material in rock phosphate ore. Their activity concentration is in the range of 0.51–1.80 Bq g^{-1}, which is considered safe (Atomic Energy Regulation Board, Government of India, New Delhi 2009). Bq (Becquerel) is the SI unit of radioactivity and referred as Bq per gram of the material. But in many countries where its radioactivity is higher, it is banned for use in making boards as well as for agricultural use.

For every tonne of phosphoric acid produced, 3.0–4.5 tonnes of phosphogypsum are generated as by-product. In India 11 million tonnes of phosphogypsum is produced annually. It is used for road building, manufacturing of bricks, wall boards, as a fertilizer for Ca and S nutrition and as a soil conditioner.

Major concern with respect to use of phosphogypsum as amendment is its fluorine content, which may range from 0.5 to 4% (Singh et al. 1980a, b; Abrol et al. 1981). When large quantities of F are added along with phosphogypsum in alkali soils, most of it is converted into NaF which is soluble, leachable and available to plants (Singh et al. 1980a, b; Chhabra et al. 1980a, b). This may contaminate the groundwater. It can also affect health of human-beings and animals consuming F-rich agricultural products. Fluorine present in phosphogypsum may also react with silicate minerals and dissolve them (Eq. 6.25).

$$\underset{\text{Silicate mineral}}{MAlSiO_2} + \underset{\text{Hydrofluoric acid}}{7HF} + nH_2O \rightarrow MO + \underset{\text{Aluminium fluoride}}{AlF_3.4H_2O} + \underset{\text{Silicon tetra fluoride}}{SiF_4} + nH_2O \qquad (6.25)$$

Where $MAlSiO_2$ represents aluminosilicate mineral and M refer to Ca, Mg, Na, K and Fe. Some of SiF_4 formed may hydrolyse to form H_2SiF_6 (Fluro silicic acid) and dissolve clay minerals even at neutral pH as in reclaimed alkali soils and accelerate leaching of contaminants into groundwater (CPCB 2012). To safeguard these concerns, Bureau of Indian Standards (1982a) has fixed the following standards for agricultural grade phosphogypsum (Table 6.24).

Table 6.24 Indian standard specifications for by-product gypsum (phosphogypsum) for use as an amendment for reclamation of alkali soils (IS10170:1982)

Particulars	Concentration, %
Calcium sulphate dehydrate ($CaSO_4.2H_2O$)	70.00
Sodium	0.75
Fluorine	1.00
Cadmium[a]	0.01
Lead[a]	0.05
Arsenic[a]	0.05
Mercury[a]	0.002
Moisture	< 15

Source: Bureau of Indian Standards (1982a)
[a]Central Pollution Control Board, India (2012)

As per chemical formula, pure fluorapatite [$3Ca_3(PO_4)_2.CaF_2$)] contains 3.77% fluorine. But RP ore may contain one or more elements like Cl, and OH within the apatite lattice. Also, it may contain $CaCO_3$, Fe- and Al-oxides, quartz, S, Mg, other alkali metals and some trace elements as impurities. Due to these reasons, F-content of the RP-ore may vary from 0.5 to about 3.5%.

To minimize F content of phosphogypsum, it is essential to defluorinate rock phosphate before production of phosphoric acid. This is done by thermal treatment in furnaces or kilns wherein RP is heated up to a temperature of 1400 °C in the presence of sand. By this way all the F is lost through volatilization. Since it increases the cost, it is done only when defluorinated-RP is used as animal feed to supplement bone meal. When it is used for H_3PO_4 production, such costly treatment is not given resulting in high F content of phosphogypsum. But considering the pollution and health risks of high F, it should be made mandatory so that F concentration of phosphogypsum is reduced below 1%.

6.4.3.2 Flue Gas Desulphurization (FGD) Gypsum

Flue gas desulphurization (FGD) gypsum also known as synthetic gypsum (SG) represents a new and large-volume source for use in reclamation of alkali soils. It is produced as a byproduct when coal is burned in power plants to produce electricity, heat, or other forms of energy. Generally, coal contains appreciable amounts of sulphur, which is converted to SO_2 and is released in the emissions, polluting the environment. To control this, SO_2 of the emission gasses is scrubbed out of the flue gases so as to successfully bring these utilities into regulatory compliance. As per the notification, in India, the SO_2 emissions are to be brought down to level of <600 mg NM^{-3} i.e. less than 600 mg of SO_2 in one normal cubic meter of air, at 25 °C temperature and 1 atm pressure.

Flue gas desulphurization (FGD) gypsum is created in limestone (Eq. 6.26), or hydrated lime-forced oxidation scrubbers that remove SO_2 from the flue gas stream after coal combustion. In general, a wet scrubbing process first exposes the flue gases to slurry of hydrated lime (Eq. 6.27). Capturing of SO_2 by the lime slurry initially forms calcium sulphite ($CaSO_2$). Forcing additional air into the system, oxidizes calcium sulphite and converts it into gypsum, i.e. $CaSO_4.2H_2O$ (Eq. 6.28).

$$\underset{\text{Limestone}}{CaCO_3(s)} + \underset{\text{Sulphur-di-oxide}}{SO_2(g)} \rightarrow \underset{\text{Calcium sulphite}}{CaSO_3(s)} \downarrow + CO_2(g) \uparrow \tag{6.26}$$

$$\underset{\text{Hydrated lime}}{Ca(OH)_2(s)} + \underset{\text{Sulpur-di-oxide}}{SO_2(g)} \rightarrow \underset{\text{Calcium sulphite}}{CaSO_3(s)} \downarrow + H_2O(l) \tag{6.27}$$

$$\underset{\text{Calcium sulphite}}{CaSO_3(s)} + 2H_2O(l) + \underset{\text{Oxygen}}{½O_2(g)} \rightarrow \underset{\text{Synthetic gypsum}}{CaSO_4 \cdot 2H_2O(s)} \downarrow \tag{6.28}$$

Quality of FGD-gypsum produced, depends upon the quality of limestone or quicklime used in the scrubbing process. Considering the chemical composition (Table 6.25), mineralogical and physical properties (Table 6.26) of FGD-gypsum

Table 6.25 Chemical properties of FGD-gypsum from the W. H. Zimmer Station of Duke Energy (Moscow, Ohio) and mined gypsum from the Kwest Group (Port Clinton, Ohio)

Elements, Unit	FGD-gypsum	Mined gypsum
Plant macronutrients		
Calcium, %	24.3	24.5
Sulphur, %	18.5	16.1
Nitrogen, ppm	970	–
Phosphorus, ppm	< 1.0	< 30
Potassium, ppm	< 74	< 3600
Magnesium, ppm	200	26,900
Plant micronutrients, ppm		
Boron	13	99
Copper	< 0.38	< 0.60
Iron	150	3800
Manganese	0.62	225
Molybdenum	3.2	< 0.60
Nickel	< 3.0	< 0.60
Zinc	1.2	8.7
Elements of environmental concern, ppm		
Arsenic	< 11	462
Barium	5.5	76
Cadmium	< 1.0	< 0.12
Chromium	< 1.0	10.4
Lead	< 5.0	100
Selenium	< 25	< 0.60

Source: Dontsova et al. (2005)

Table 6.26 Mineralogical and physical properties of FGD-gypsum and mined gypsum

Properties	FGD gypsum	Mined gypsum
Minerals present	Gypsum, quartz	Gypsum, quartz, dolomite
Water content, %	5.5	0.38
Purity as $CaSO_4.2H_2O$, %	99.6	87.1
Insoluble residue, %	0.4	13
Particle size		
> 250 microns, %	0.14	100
150–250 microns, %	3.2	0
105–150 microns, %	33	0
74 – 105microns, %	33	0
< 74 microns, %	31	0

Source: Dontsova et al. (2005)

and mined gypsum, synthetic gypsum is of high quality and suitable for industrial (e.g. manufacturing of wallboard) and agricultural uses (Chen and Warren 2011). FGD-gypsum usually possesses a much smaller and more uniform particle size (more than 95% are of <150 microns) than mined gypsum that has to be granulated to produce a final size of 2–4 mm. FGD-gypsum produced in India has purity of

more than 80–90% as $CaSO_4.2H_20$, with fineness of 100% passing as 200 microns. However, mined gypsum contains more of Mg, K and Fe as compared to FGD-gypsum. Air-dry FGD-gypsum contains 5–10% moisture.

Considering the environmental concerns, large volumes of such by-product gypsum will be produced in future in all the countries using coal-fired thermal plants. In India alone it is estimated that FGD generated gypsum by power sector is going to be approximately 23 MT per year (Satyamurthy 2019). These FGD systems are generating large quantities of gypsum in the USA, Canada, Australia, Europe and other industrialized countries which must be placed in landfills, deposited in surface impoundments, or used as an agricultural amendment (Dontsova et al. 2005). Extensive reclamation of saline-sodic soils using FGD-gypsum has been successfully undertaken in Songnen Plain, NE China (Zhao et al. 2018). FGD-gypsum is also used by cement industry as a substitute for mineral gypsum.

6.4.3.3 Press Mud

Press mud also known as **filter cake** is an industrial waste available from sugar mills. It is a residue left after filtration of clarified sugarcane juice. For every 10 tonnes of sugarcane crushed, about 3 tonnes of press mud are left behind as by-product. India, China and Brazil together account for about 75% of the world's sugar production and produce large volumes of press mud. It is estimated that on an average, each tonne of press mud contains 10–15 kg N, 36 kg P, 14 kg K and 23 kg S along with appreciable amounts of secondary and micronutrients (Tondon 1992). Typical composition and nutrient content of press mud are given in Tables 6.27 and 6.28, respectively (Gupta et al. 2011).

Sulphitation press mud being acidic in nature is used for reclamation of alkali soils (Yaduvanshi and Yadav 1990) whereas carbonation press mud being alkaline in nature is useful to reclaim acid soils (Solaimalai et al. 2001). Sulphitation process is carried out with quick lime (CaO) and sulphur–di-oxide (SO_2) which form $CaSO_4$ (Eq. 6.29) in situ. While in carbonation process, quick lime and carbon-di-oxide are used which form $CaCO_3$ (Eq. 6.30) in situ. Carbonation process is mostly used to

Table 6.27 Typical composition of sulphitation press mud

Parameters	Concentration, %
Sugar	5–15
Fibre	15–30
Crude wax	5–14
Crude protein	5–15
SiO_2	4–10
CaO	1–4
MgO	0.5–1.5
K_2O	1–3
Total ash	9–10

Source: Gupta et al. (2011)

Table 6.28 Nutrient content of press mud

Nutrients	Concentration, %
Nitrogen	1.9
Phosphorus	1.8
Potassium	0.9
Calcium	4.3
Magnesium	0.7
Sulphur	3.2
Sodium	0.1
Manganese	0.034
Zinc	0.008
Copper	0.053

Source: Gupta et al. (2011)

clarify sugar beet juice in Europe, America and Western countries. These processes help in removing colour and coagulate colloidal impurities from the cane / sugar beet juice. On filtration, these are recovered as residues, together with flocculated colloidal impurities, cane-wax, pectin, colouring mater, dispersed soil particles and bagasse in the form of press mud.

$$\underset{\text{Quick lime}}{2CaO} + \underset{\text{Sulphur-di-oxide}}{2SO_2} + O_2 \rightarrow \underset{\text{Calcium sulphate}}{2CaSO_4} \tag{6.29}$$

$$\underset{\text{Quick lilme}}{CaO} + \underset{\text{Carbon-di-oxide}}{CO_2} \rightarrow \underset{\text{Calcium carbonate}}{CaCO_3} \tag{6.30}$$

Since, quality of press mud varies from mill to mill and even on day-to-day basis within the same mill, Bureau of Indian Standards, New Delhi, India (2003) has established the following standards for its use in agriculture (Table 6.29).

For reclamation of alkali soils, effectiveness of press mud from carbonation process which contains about 70% of Ca as $CaCO_3$ and 11.0% OM, is very poor in comparison with that of gypsum (Kanwar and Chawla 1963; Milap Chand et al. 1977 (Table 6.30); Chhabra et al. 1992).

Press mud from sulphitation process contains 9.3% $CaSO_4$ and 35.8% organic matter. Because of its high OM, sugars and nutrient content, press mud is also used as fertilizer as well as food ingredient for ruminants. Its application improves soil physical, chemical and biological properties and enhances crop yield and quality. In many cases, press mud because of its high calorific value (ranging from 1000 to 3600 kcal kg^{-1} depending upon the moisture and ash content) is burnt in kilns to replace coal and firewood resulting in loss and wastage of millions of tonnes of nutrients.

Table 6.29 Indian standard specifications for press mud for agricultural use (IS 15343:2003)

Parameters	Value
Organic carbon	Not less than 20%
C:N ratio	25:1
Calcium	0.5%
Phosphorus as P_2O_5	2.5%
Sulphur as SO_4^{2-}	2.5%
pH (1:10)	7.5
EC (1:10)	4.00 dS m^{-1}
Moisture	Not more than 30%

Source: Bureau of Indian Standards (2003)

Table 6.30 Effect of different amendments on yield of barley grown in a highly sodic soil

Amendments	Barley grain yield, t ha^{-1}
Control	0.02
Gypsum[a]	3.10
Sulphuric acid[a]	3.20
Aluminium sulphate[a]	3.12
Ferrous sulphate[a]	2.62
Farm yard manure[b]	0.29
Press mud (C)[c]	0.10
Press mud (S)[c]	0.61

Source: Milap Chand et al. (1977)
[a]Average yield for three levels of application, *viz.* 33, 66, and 100% GR
[b]FYM was applied @ 15, 30 and 45 t ha^{-1}
[c]Press muds were applied @10, 20 and 30 t ha^{-1}

6.4.3.4 Activated Press Mud

Activated press mud (APM) also known as bio-composted press mud is another by-product of sugar mills, prepared from composting of press mud with distillery spent wash using microbial cultures (Table 6.31, Sarangi et al. 2005) which can be used as an amendment for reclamation of alkali soils. In this process, bio-non-degradable portion of press mud such as cellulose, lignin and waxes etc. get converted into humus which further enriches the soil. In addition to this it utilizes the spent wash which is another pollutant of environment.

6.4.3.5 Petroleum Sulphur

Sulphur is a natural element contained in crude oil, naphthas, and petroleum products. Since it is one of the hazardous air pollutants, efforts are made to remove S from the petroleum products especially from those used as vehicle fuel and furnace

Table 6.31 Physico-chemical characteristics of activated press mud

Parameters	Value
pH	7–8
EC, dS m^{-1}	1–1.4
Colour	Light brown
Calcium, %	4.3–5.0
Sodium, %	0.5–0.7
Bicarbonates, %	0.005–0.007
Carbonates, %	0.001–0.002
Chloride, %	0.01–0.02
Sulphate, %	0.1–0.2
Organic C, %	15.98
Total N, %	1.27
Available N, %	0.11
Total P, %	1.61
Total K, %	1.42

Source: Sarangi et al. (2005)

oil. The oil refining process commonly includes hydro-de-sulphurization which converts most of the S found as a part of petroleum component like ethanethiol into gaseous hydrogen sulphide (Eq. 6.31). It is highly toxic gas with an irritating smell of rotten eggs.

$$\underset{\text{Ethanethiol}}{C_2H_5SH} + \underset{\text{Hydrogen}}{H_2} \rightarrow \underset{\text{Ethane}}{C_2H_6} + \underset{\text{Hydrogne sulphide}}{H_2S} \tag{6.31}$$

Raw natural gas also contains gaseous H_2S and other S-containing components which are removed in the processing plants before the gas is distributed to consumers. Hydrogen sulphide gas, so removed is converted into by-product elemental sulphur in Claus plants. The reaction proceeds in two steps (Eqs. 6.32 and 6.33):

$$\underset{\text{Hydrogen sulphide}}{2H_2S} + \underset{\text{oxygen}}{3O_2} \rightarrow \underset{\text{Sulphur di-oxide}}{2SO_2} + 2H_2O \tag{6.32}$$

$$\underset{\text{Hydrogen sulphide}}{4H_2S} + \underset{\text{Sulphur di-oxide}}{2SO_2} \rightarrow \underset{\text{Elemental sulphur}}{3S_2} + 4H_2O \tag{6.33}$$

By-product S is a yellow-coloured crystalline material and is used as raw material for manufacturing of industrial H_2SO_4. It is highly reactive and forms corrosive H_2SO_4 in the presence of moisture and air. It is now available for use as amendment for reclamation of alkali soils and production of single superphosphate.

The by-product S from oil refineries comes in the form of "High Purity Prill Sulphur" (3–5 mm dia., 99.9% purity) and sulphur cake (6–12 mm, 55–65% purity). Sulphur prill is made from sulphur which is recovered from the vapor state by condensation. Sulphur cake is solid elemental sulphur produced through an iron-based liquid redox system. Because of its large size, S-release from it is very slow

and its oxidation to H_2SO_4 is very poor. It has to be first grounded to produce S-powder (Particle size <5 mm) so as to be more reactive. But this increases the cost and thus makes it more expensive. Its efficiency as an amendment for alkali soils *vis-à-vis* gypsum is still to be demonstrated under field conditions.

6.4.3.6 Fly Ash

Fly ash (FA) is a waste product of the thermal electric power plants where coal is used as a source of fossil fuel. India alone is producing about 176.74 million tonnes of fly ash, out of which only 60.97% is being utilized for various purposes (CEAI, 2015–16). It is used in manufacturing of environment friendly products like bricks and cement for construction of buildings; as filling material in embankment of roads and flyovers, low-lying areas and backfilling of mine voids etc. It can also be a good material (physical amendment) for improving physical properties of heavy textured soils and reclamation of acid and alkali soils.

Reaction of fly ash varies from acidic to basic depending upon the source of coal, mainly its S- content, which in turn depends upon its origin. Acidic fly ash can act as amendment for alkali soils while the basic fly ash can be used as amendment for reclamation of acid soils. Chemical characteristics (Table 6.32) of fly ash depend upon the type of coal used, method of collection and storage. Fresh fly ash collected directly from the kiln contains high amount of soluble salts. Fly ash collected and carried to the dumpsite through water contains fewer amounts of soluble salts as those are washed out during this process.

Table 6.32 Chemical composition of fly ash collected from the dump yard of Panipat Thermal Plant, Haryana, India

Characteristics	**Value**
pH_2 (1:2 suspension)	5.95
EC_2 (1:2 suspension), dS m^{-1}	0.45
Available nutrients	
N, ppm	Nil
K,,,	41.30
P,,,	11.00
Zn,,,	0.91
Fe,,,	20.23
Mn,,,	1.36
Cu,,,	0.46
Toxic elements	
Cd, ppm	Nil
Ni,,,	Nil
Cr,,,	Nil
Pb,,,	Nil

Source: Chhabra and Khajanchi Lal (2007)

Fly ash, basically is an amorphous (because of its rapid cooling in the kiln) ferro-aluminium silicate and contains all naturally existing elements except nitrogen and organic carbon. Major matrix elements found in fly ash are Si, Al, Fe together with Ca, K, Mg, Na, P and S in the form of SiO_2 = 53.39%; Al_2O_3 = 16.07%; F_2O_3 = 13.05%; CaO = 6.33%, MgO = 5.48%; SO_4 = 1.06% and Na_2O = 1.59%. Depending upon the source and quality of coal used, it may contain micronutrients like Zn, Mn, Cu, Fe and Mo; and sometimes appreciable quantities of toxic metals like Pb, Ni, Cd and chromium. Its pH may vary from slightly acidic to neutral. However, being inert material, it has very low buffering capacity. It is a rich source of Si and potassium. It has high water holding capacity varying from 29.6 to 42.4% at saturation and 13.4% at 1/3 bar. Its bulk density varies from 1 to 1.8 g per cm^{-3} (Chhabra and Khajanchi Lal 2007). The major pollution hazard of fly ash is due to its fine particles, < 0.1 mm dia., which are about 25.39% of the total weight (Table 6.33). These are in loose form and increase the suspended particle-load (SPL) of air, especially during dry, windy summer months. Breathing in such fine particle loaded-air, over long periods, causes lungs related diseases like asthma and bronchitis; cancer and skin diseases like allergies. Apart from being health hazards for human-beings and animals, these suspended particles make a fine coating on leaf surfaces restricting their photosynthetic activities.

Response of crops and effect on soil properties depends upon the characteristics of fly ash, rate of its application, soil type and the nature of crop. Mahalingam (1973) observed sustained increase in rice yields by applying low rates (2–4% w/w) of fly ash in saline and alkali soils. Results of field experiments (Table 6.34; Chhabra and Khajanchi Lal 2007) conducted on calcareous reclaimed alkali soil (pH_2 8.60, EC_2 0.243 dS m^{-1} of surface 15 cm soil), showed that there was neither a beneficial nor a detrimental effect of fly ash applied up to 50 t ha^{-1} continuously for 3 years, on yield of rice and wheat crops. Fly ash, collected from Panipat thermal plant, India was applied @ 0, 2.5, 5.0, 7.5, 10.0, 20.0, 30.0, 40.0 and 50.0 t ha^{-1} either once or continuously for 3 years before transplanting rice.

Plant height, number of tillers, grain yield, straw yield, grain:straw ratio and 1000 grain weight of both rice and wheat crops were not affected by application of fly ash. Not only the agronomic attributes but also the chemical composition (Na, K, Ca, Mg, P, Zn, Fe, Mn, and Cu) including the toxic elements like Pb, Ni, Cr and Cd of

Table 6.33 Mechanical analysis of fly ash obtained from Panipat Thermal Plant, Haryana, India

Size of the fraction	% fraction
>2.00 mm	01.10
2.00–1.00 mm	00.36
1.00–0.50 mm	03.88
0.50–0.25 mm	16.15
0.25–0.10 mm	53.12
0.10–0.05 mm	23.35
< 0.05 mm	02.04

Source: Chhabra and Khajanchi Lal (2007)

Table 6.34 Effect of fly ash application continuously for 3 years on grain yield of rice and wheat in a reclaimed alkali alluvial soil

	Grain yield, t ha^{-1}					
	First year		Second year		Third year	
Amount of fly ash applied, t ha^{-1}	Rice	Wheat	Rice	Wheat	Rice	Wheat
0	5.833	4.457	5.236	4.497	5.667	4.855
2.5	5.776	4.497	5.428	4.651	5.671	4.988
5.0	5.845.	4.497	5.401	4.746	5.583	4.871
7.5	5.947	4.260	5.595	4.644	5.504	4.805
10.0	5.823	4.550	5.580	4.536	5.515	4.838
20.0	5.967	4.230	5.496	4.421	5.721	5.032
30.0	5.852	4.230	5.322	4.325	5.670	5.128
40.0	5.871	4.270	5.377	4.565	5.558	5.128
50.0	5.668	4.303	5.222	4.506	5.639	5.128
Mean	*5.842*	*4.366*	*5.406*	*4.543*	*5.614*	*4.975*
LSD at P = 0.05	NS	NS	NS	NS	NS	NS

Source: Chhabra and Khajanchi Lal (2007)

grain and straw were not affected by such a high level of fly ash application (Tables 6.35 and 6.36). However, there was a gradual increase in Si content of grain and straw of rice, with increase in level of fly ash application. In rice straw, it increased from 6.317% in control to 8.207% when 50 t ha^{-1} of fly ash was applied every year. In rice grain it increased from 1.022% in control to 1.340% at fly ash level of 50 t ha^{-1}. Though Si concentration in rice grain and straw increased with increase in the level of fly ash, the increase was not significant beyond fly ash level of 20 t ha^{-1}. Mongia et al. (2003) suggested that fly ash can be used as a source of Si for increasing rice productivity on reclaimed alkali soils. Similarly, it can be used as a source of silicon for Si-loving crops like sugarcane, barley, and grasses etc. Their results suggested that fly ash of thermal power stations like that of Panipat, India which do not contain appreciable amounts of DTPA-extractable toxic elements can be safely disposed of on reclaimed alkali soils without any adverse effect on yield and quality of both rice and wheat crops. Khajanchi Lal et al. (2012) observed an increase in K content of rice crop on application of fly ash.

Sikka and Kansal (1995) reported a positive response of both rice and wheat crops to application of fly ash (2–4% w / w) on a neutral soil. Grain yield of paddy increased from 6.18 to 6.36 and that of wheat from 3.94 to 4.26 t ha^{-1} by application of fly ash from 0 to 80 t ha^{-1}. Fly ash has positive effect on growth of berseem (*Trifolium alexandrinum*) mainly due to increased availability of Mo which is essential element for this crop. Kene et al. (1991) found a significant reduction in total and available N and P of soil by application of fly ash @ 15% (w / w).

There was a significant effect of FA application on bulk density (BD) of surface soil layers (Fig. 6.5). In 0–5 cm soil depth, it decreased from 1.335 in control to 1.270 g cm^{-3} in treatment receiving fly ash @ 50 t ha^{-1}. Similar trend was observed in soil depth of 5–10 and 10–15 cm soil layers. Significant effect of FA on

Table 6.35 Effect of different amounts of fly ash applied continuously for 3 years on chemical composition, mg kg^{-1}, of rice grain

Amount of fly ash applied, t ha^{-1}	P	K	Na	Ca	Mg	Zn	Fe	Mn	Cu	Pb	Cd	Ni	Si
0	2280	1665	121	254	2168	16	27	20	5.5	Nil	Nil	Nil	10,220
2.5	2330	1649	121	236	2190	14	28	25	5.1	,	,	,	12,080
5.0	2320	1665	131	231	2182	14	26	20-	6.2	,	,	,	12,080
7.0	2330	1699	112	247	2245	14	29	20	5.5	,	,	,	12,080
10.0	2410	1680	121	251	2462	15	29	23	5.4	,	,	,	12,080
20.0	2520	1738	131	234	2313	15	28	23	6.3	,	,	,	13,120
30.0	2500	1695	131	249	2418	15	26	23	5.9	,	,	,	13,290
40.0	2480	1727	140	254	2359	16	30	22	5.7	,	,	,	13,610
50.0	2450	1711	140	254	2291	16	31	23	5.4	,	,	,	13,400
LSD at P = 0.05	NS	NS	NS	NS	NS	NS	NS	NS	NS	–	–	–	1930

Source: Chhabra and Khajanchi Lal (2007)

Table 6.36 Effect of different amounts of fly ash applied continuously for 3 years on chemical composition, mg kg^{-1}, of rice straw

Amount of fly ash applied, t ha^{-1}	P	K	Na	Ca	Mg	Zn	Fe	Mn	Cu	Pb	Si
0	950	17,438	1144	2711	7149	42	422	262	3.0	34	63,170
2.5	910	17,766	1473	2885	7297	44	419	274	3.0	32	63,800
5.0	870	17,786	1125	2895	7207	41	456	254	3.8	40	68,800
7.0	910	17,392	1230	2713	7193	42	459	253	2.9	35	66,100
10.0	940	17,879	1296	2857	7171	43	454	262	3.1	39	72,600
20.0	900	18,528	1190	2740	7247	46	413	239	3.3	36	79,400
30.0	920	17,978	1518	2771	7109	42	431	260	3.0	32	79,930
40.0	930	17,926	1209	2698	6792	41	416	263	2.8	34	77,530
50.0	920	17,712	1366	2748	6807	46	409	259	3.6	32	82,070
LSD at P = 0.05	NS	NS	NS	NS	NS	NS	NS	NS	NS	–	10,870

Concentration of Cd and Ni was nil
Source: Chhabra and Khajanchi Lal (2007)

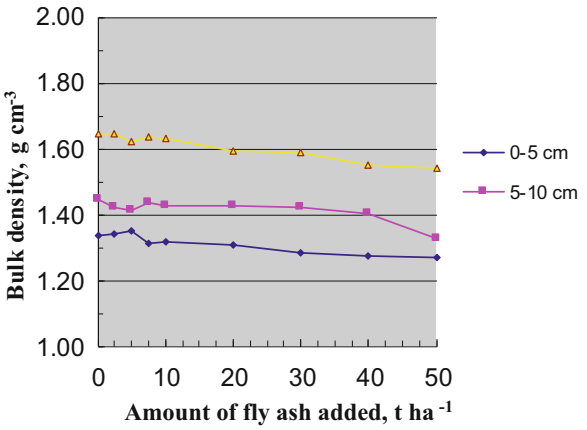

Fig. 6.5 Effect of fly ash applied continuously for 3 years on bulk density of different depths of an alluvial soil under rice - wheat cropping system (Chhabra and Khajanchi Lal 2007)

decreasing BD was observed only after the level of 20 t ha^{-1}. The decrease in BD of soil was due to physical mixing of FA, which had a BD of 1.0748 against the value of 1.3367 g cm^{-3} of the original soil. Since, fly ash was applied on surface and mixed in shallow depths, its beneficial effect on decreasing BD was visible to a depth of 15 cm. But when applied at higher levels of 50 t ha^{-1}, even BD of soil to a depth of 30 cm was affected. Infiltration rate measured in situ showed that it increased with increase in the level of fly ash application (Fig. 6.6). The differences were more striking in first 1 h and were maintained even up to 72 hours of study. In first 15 minutes itself, depth of water intake was 1.249 cm in control, which increased to

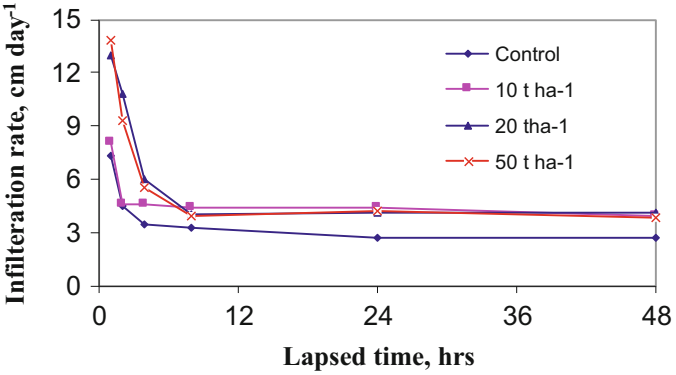

Fig. 6.6 Effect of fly ash applied for 3 years on infiltration rate of an alluvial reclaimed alkali soil (Chhabra and Khajanchi Lal 2007)

1.695 in 20 t ha^{-1}, and 1.982 cm in plots treated with 50 t ha^{-1} fly ash. There were no significant differences in cumulative water intake in treatments up to 10 t ha^{-1} fly ash. Though it increased with increase in level of fly ash, there were no significant differences among the higher levels also.

From crop yield data, chemical composition of grain and straw and results on physical properties of soils, Chhabra and Khajanchi Lal (2007) concluded that fly ash of thermal power stations like that of Panipat, India, though did not have any beneficial effect on soil pH and EC of reclaimed alkali soils, yet can be safely disposed of without any adverse effect on both rice and wheat crops and any harm to soil. Application of fly ash improves soil physical properties which in turn help in improving infiltration rate, leaching of salts, aeration and water holding capacity of the heavy textured soils and of physically deteriorated alkali soils. This will also save large areas of fertile lands which otherwise have to be taken out of cultivation to make additional dumps for storing this ever-increasing waste material.

6.4.3.7 Biochar

Biochar is a solid carbonaceous residue left after slow pyrolysis of organic matter at 600–700 °C in N_2 environment in a retort or converter to produce bio fuel (Lehmann 2007). When organic biomass is heated in a closed container in the absence of oxygen, the organic matter chemically decomposes (due to heat) producing pyrolytic gases and vapours, which reunite and condense to produce black liquid called tar, from which bio fuel is produced through distillation. The left-over solid residue, about 10–20% of the original biomass, containing carbon, ash and nutrients is called by-product biochar. The propagators of bio fuel technology are advocating that the major land areas in the developed countries should be put under tree farming. The biomass produced is to be used for the production of renewable energy i.e. bio fuel

and the carbon-rich residue, biochar is to be used along with chemical fertilizers to enrich soil of its organic matter and sequestering of atmospheric carbon and thus arrest the climate change.

Considering its potential uses, biochar is now being produced, as main component by intentionally carbonization through smouldering of organic wastes in modified low-cost kilns at temperatures below 270 °C, just like manufacturing of charcoal. In this system, yield of biochar is more, about 70–80%, depending upon the temperature, but no tar or oil is produced. For this, organic materials like agricultural residues [(rice straw, husk; sunflower, cotton and pigeon pea stalks; corn cobs, maize stover, groundnut shells (husk), coffee husk, pistachio shells, orange peel, switchgrass (*Panicum virgatum*), etc.]; industrial wastes like sugarcane and sugar beet bagasse, press mud, waste from corn starch industries, spent grain from breweries etc.); woody biomass from trees (wood from bamboo, eucalyptus, poplar, pine, willow and oak trees; bark, loppings, waste from plywood industry, wood chips, sawdust, pine needles etc.); FYM, city compost and waste materials like poultry droppings, sludge etc. can be used. Instead of burning these materials as such in the field and polluting environment or using these for producing heat energy as in boilers or brick kilns, it is 3–9 times more efficient to produce energy in the form of bio fuel and biochar through pyrolysis (Lehmann 2007). It is a carbon-negative technology which minimizes air pollution and at the same time sequesters plant carbon in soil (Laird 2008). This process also reduces volume and weight of the bulky agricultural biomass and converts it in to value added biochar, easy to store and handle in field.

Biochar is also called pyrogenic carbon, black carbon, or dead carbon. It is stable form of carbon and lasts for thousands of years in soil. It is different from humus which is called the living carbon and is essential for biological life of soil, granulation and also for enhancing availability of many plant nutrients through the process of chelation or complex formation.

Biochar is made up of C, H, S, O and nitrogen. Depending upon the manufacturing process, its carbon content varies from 60 to 80%. It contains minerals and ash fraction of the biomass from which it is produced. Biochar's pH ranges from acidic to alkaline (5.9–12.3), depending upon the nature of the biomass used (Chan and Xu 2009) and temperature during pyrolysis (Ippolito et al. 2016). pH of biochar produced from poultry droppings (chicken litter) is alkaline while that produced from wood shavings have acidic-pH. Biochars produced from non-woody feedstocks such as plant residues and manures are richer in nutrients and have higher pH as compared to those derived from lignocellulosic materials such as wood (Mukherjee and Zimmerman 2013). Properties of biochar depend upon quality of the biomass and processing parameters (Rawat et al. 2019). Biochars produced at temperatures below 400 °C have low pH, low CEC and surface area (Ippolito et al. 2016). In general, biochar is highly porous (porosity being 50–80%), finely grained, light weight, and have high surface area with high CEC as well as high AEC (Lawrinenko and Laird 2015).

Various studies done under controlled conditions have shown that when used as an amendment, it improves soil quality, reduces leaching losses of added fertilizer-

anionic nutrients (NO_3^-, $H_2PO_4^-$ and SO_4^{2-}) and increases their availability (Glaser et al. 2002; Mukherjee and Zimmerman 2013; Mukherjee et al. 2014; Laird 2008). Due to its high surface charge density, it increases CEC and overall sorption capacity to retain nutrients (Glaser et al. 2002; Kanthle et al. 2016). Because of its acidic surface functional groups, it also increases AEC (Singh et al. 2010; Kameyama et al. 2012). Its application improves soil physical properties like reduction in bulk density, increase in hydraulic conductivity and aggregate stability (Herth et al. 2013; Ouyang et al. 2013), porosity (Novak et al. 2012; Ouyang et al. 2013; Yu et al. 2013; Basso et al. 2013), water retention (Jones et al. 2012), water holding capacity and thus water availability for crop use. Most of biochars have relatively low bulk density, generally <0.6 g cm^{-3}, and due to this, their addition improves bulk density of soil (Chen et al. 2011; Jones et al. 2012). In acidic soils, its addition increases pH, reduces Al-toxicity and increases availability of nutrients (Glaser et al. 2002). Rawat et al. (2019) reported positive effect of biochar on crop yield with rates of 5–50 t ha^{-1} and appropriate nutrient management. Higher doses of biochar may result in decreased yields mainly due to induced N-deficiency. However, very few studies have been conducted to prove its effectiveness under field conditions and that too for salt-affected soils.

Application of biochar as an amendment for alkali soils which have problems of both physical and chemical properties can be very encouraging. Acidic biochar can reduce high pH of alkali soils and dissolve $CaCO_3$ (Ippolito et al. 2016) to provide soluble-Ca for lowering ESP. In the laboratory study, addition of biochar significantly reduced ECe, ESP, SAR and increased exchangeable cations of a saline-sodic soil. In a pot experiment, Feng et al. (2018) observed decrease in Na accumulation in plant and increase in rice yield by application of biochar in a saline-sodic soil. It also accelerated salt-leaching and thus decreased the time required for reducing salt concentration in the rhizosphere. Normally, biochar fractions <2 mm size are used as soil amendment. Yu et al. (2019) reported that application of biochar improves crop production in problem soils. In the laboratory, its effect on soil properties have been studied after application of 1–2% (w/w) (Herth et al. 2013).

Biochar acts as modifier of the rootzone salinity. Due to sorption of soluble salts, phytotoxic metals and pesticides, biochar helps in decreasing their effective concentration in the rhizosphere and thus helps plants to avoid their deleterious effects at critical stages of germination and early establishment. Its high porosity and physical structure make it an excellent habitat for organisms already present in soil and helps them to proliferate.

In addition to permanently sequestering carbon, biochars release nutrient elements and thus, are beneficial to plants when amended in soils (Laird 2008). It prevents pollution of groundwater by minimizing leaching of nutrients. It also decreases pollution of runoff water by retaining these nutrients in soil (Lehmann et al. 2003). Addition of biochar in soil also decreases emission of potent greenhouse gasses (GHG) like nitrous oxide (NO2) and methane (CH4) (Rondon et al. 2005; Zhang et al. 2010).

Considering its beneficial role in improving physical and chemical properties of soil, increase in water retention, decrease in leaching losses of nutrients, reduction in

ECe, ESP and SAR of soil, increase in soil carbon, reduction in emission of GHG, biochar seems to be a potential organic amendment for salt-affected soils.

However, most of the findings are based on short-term controlled laboratory and greenhouse studies involving diverse type of biochar produced at different pyrolysis temperatures. Considering large variations lin properties (pH, CEC, AEC, SA etc.) of biochar, it is important to match the properties of biochar with the need of soil. An increase in soil pH by application of biochar amendment may adversely affect the nutrient availability and crop growth in neutral and alkali soils (Kishimoto and Sugiura 1985; McElligott et al. 2011; Xu et al. 2012). Hardwood fast pyrolysis biochar did not affect CEC of sandy loam soil (Basso et al. 2013). Instead of immediate response in the first season, full beneficial effects of biochar on soil properties may occur over a long period (Mukherjee and Lal 2014). Polycyclic aromatic hydrocarbons (PAHs) are present in varying amounts in biochar which can increase their level in soil. Unless sorbed or decomposed, toxicity of biochar-born PAHs can pose serious threats to the rhizosphere processes. It may increase PAHs content of crops and thus pose serious health risk to human-beings. It is perceived that biochar increases surface area of soil due to its high porosity. But over the period porosity of biochar may decrease due to clogging of pores or and precipitation of absorbed salts. Improvement in physical properties by addition of biochar may not be the same for all soils.

Due to increase in pH and toxic effects of high levels of salts and heavy metals accumulated in biochar (Kilham 1985), its application may have a negative effect on VAM population (Gaur and Adholeya 2000; Birk et al. 2009). Hardwood biochars, produced at high temperature, have negative effect on earthworm population (Gomez-Eyles et al. 2011). Though in most cases application of biochar may increase crop yields yet in some cases there may be a negative effect on growth and yield. This may be due to induced deficiency of N and micronutrients. There are also contradicting reports on the emission of GHG on application of biochar (Rondon et al. 2005; Spokas et al. 2009). Biochars produced from municipal and industrial sludges may contaminate soil from heavy metals and thus may be environmentally not safe. Production of biochar in conventional kilns is not pollution free as during the process of pyrolysis, which is basically incomplete combustion, there is substantial emission of CO_2, CO, methane, nitrous oxides, and non-methane volatile organic components. Mukherjee and Lal (2014) have highlighted the various issues regarding dilemma of biochar use in agriculture. Biochar production is time- and labour- consuming and costs money.

Hence, further research on the following points is needed before it can be recommended for large scale field adoption for reclamation of alkali soils.

(i) Optimum amount and relative efficiency of biochar as an amendment for the given alkali soil.
(ii) Rate of decomposition of biochar due to biotic and abiotic processes in salt-affected soils.
(iii) Changes in properties of biochar with time.

(iv) Standardization of technology for production of biochar with respect to kind of biomass and the pyrolysis temperature suitable for the given soil type.
(v) Affordable cost of biochar production.

6.4.4 Physical Amendments

When texture of soil is heavy, addition of sand or silt from riverbed and fly ash from coal-fired thermal plants may improve its infiltration rate and thus leaching of soluble salts and the reaction products. Such inert materials, which improve physical properties of soils, are called physical amendments or soil physical conditioners. Mathur et al. (1983) observed a beneficial effect of sand applied together with gypsum on leaching of salts and yield of cotton and sorghum in salt-affected soils of Rajasthan, India. Addition of highly resistant organic materials like rice husk (Khosla 1976) and wood chips can also help in providing open channels and thus improve water infiltration rate and aeration in highly dispersed alkali soils.

Application of Krilium (Quastel 1953) and other synthetic water-soluble polyacrylamide (PAM) soil conditioners like poly vinyl alcohol, sodium alginate, a vinyl acetate-maleic acid co-polymer (VAMA) and polyacrylic acid (Allison and Moore 1956) can help in stabilizing the existing soil aggregates, cement loose clay particles together and thus improve physical properties of alkali soils. Thereby, these increase pore space, improve water infiltration into soil, prevent soil crusting (Wallace and Wallace 1990), make soil friable and easy to cultivate. This can improve germination of crops like mustard, cotton and pearl millet, which is critical in salt-affected soils. Krilium, is a synthetic polyacrylamide soil conditioner commonly known as "swell gel" [$(C_3H_5NO)_nCH_2–HC–C=O–NH_2$)]. Dextran (polysaccharide derived from condensation of glucose with chemical formula [$H(C_6H_{10}O_5.OH)$] is another high molecular weight soil conditioner which helps in binding of soil particles (Novak et al. 1955). It is also used as flocculating agent to remove organic content from raw waters. Spray of coal tar, a bituminous material, normally used for stabilizing sand dunes can also be used to promote soil aggregation. Improving soil physical properties indirectly help in better nutrition of crops and improve efficiency of applied fertilizers. Use of PAM further enhances the effectiveness of chemical amendments in reclaiming alkali soils.

Amendments are useful where soil permeability is poor because of low salinity i. e. when electrolyte concentration of the leaching water is less than the threshold concentration, or when dispersion of soil colloids is more due to high ESP, or high SAR or high RSC of the irrigation waters. But amendments will not be helpful if poor permeability is due to heavy soil texture, soil compaction, impervious layers (hardpans, claypans), soil stratification or high-water table. If the crop is receiving adequate water for near maximum yield, addition of amendments will not increase yield but may make water management a little easier, though at an additional cost of amendment including its transport, handling and application.

6.5 Gypsum Requirement

Gypsum requirement (GR) is a chemical property of a given depth of soil and refers to the requirement of pure gypsum to reduce its ESP to less than 15. Gypsum requirement depends upon initial ESP, CEC, buffering capacity of soil (texture and type of clay minerals); depth of soil to be reclaimed, amount and nature of soluble salts present in the soil. Gypsum requirement can be calculated from the data on CEC and ESP of the soil. For example, if ESP of soil is 70 and CEC is 25 me 100 g^{-1}, then to reduce ESP to 15, one will require to replace [(70–15)/100] × 25 = 13.75 me Na^+ 100 g^{-1} soil. For this one will need 13.75 me of Ca^{2+} 100 g^{-1} soil or 13.75 × 1.926 = 26.48 t of pure gypsum per hectare for 15 cm depth of soil.

6.5.1 Determination of GR

For one milliequivalent (me) of Na^+ to be replaced, one needs one me of Ca^{2+}. This amounts to 0.02 g Ca 100 g^{-1} soil or 0.86 g of pure $CaSO_4.2H_2O$ per kg soil i.e. [(172 × 0.2) ÷ 40]. Taking 2.24 × 10^6 kg as average weight of 0–15 cm soil layer, this amounts to 1.926 t of gypsum per ha per me of Na^+ to be replaced.

Puri (1934) gave a simple and direct method of determining total exchangeable-Na^+ by extracting a known weight of soil with $(NH_4)_2CO_3$ solution and then analysing sodium in the filtrate. From that, one can calculate equivalent amount of Ca^{2+} required and then the amount of gypsum to reclaim the given soil.

In laboratory, GR of soil is determined by Schoonover (1952) method. This involves equilibrating a known weight of air-dry soil with a known large volume of saturated gypsum solution and determining, by back titration, me of Ca^{2+} adsorbed by soil from the solution. However, GR determined by this technique comes out to be very high, 30 to 60 t ha^{-1} for 0–15 cm soil, and is beyond the economic means of farmers. Abrol et al. (1975) reported that soluble Na_2CO_3 of soil partially inactivates the added Ca^{2+} and thus overestimates GR in the Schoonover's method. They suggested determining GR on salt-free soil i.e. after leaching the soil with 60% alcohol, so as to get realistic estimates.

6.5.2 pH and Gypsum Requirement

Because of ease, pH of soil is measured on 1:2 soil water suspensions in most of the laboratories. In alkali alluvial soils of the Indo-Gangetic plains, there exists a good relationship between pH_2 and pHs of saturation paste (Fig. 5.9) which in turn is well correlated with ESP of soil (Fig. 5.8). Using these relationships, ESP of soil can be estimated from pH_2 and from that GR can be calculated. Further, it has been

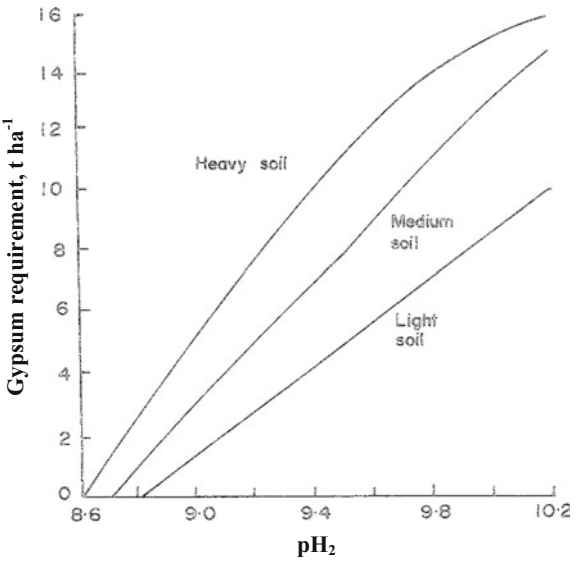

Fig. 6.7 Relationship between pH_2 and gypsum requirement of alkali alluvial soils (Abrol et al. 1980)

observed (Abrol et al. 1980) that for soils of the Indo-Gangetic plains, there exists a good relationship between pH_2 and GR of soil (Fig. 6.7). Such a relationship can form a sound basis for estimating gypsum requirement of soils of different texture and CEC. Such a "ready reckoner" can be prepared for quick recommendations of GR by each soil testing laboratory for soils existing in their area. However, such relationships should be thoroughly standardized, separately for each group of soils and for different texture, mineralogy, organic matter content and climatic conditions.

6.5.3 Efficiency of Gypsum and Nature of Soluble Salts

All alkali soils contain measurable amounts of soluble $NaHCO_3$ and Na_2CO_3 which react with the added gypsum to neutralize and precipitate soluble calcium as partially soluble $Ca(HCO_3)_2$ and insoluble $CaCO_3$ (Eqs. 6.34 and 6.35), before it can be used to replace exchangeable-Na^+. This decreases its efficiency and increases the amount of gypsum needed to reclaim the soil.

$$\underset{\text{Soluble salt in alkali soils}}{2NaHCO_3} + \underset{\text{Gypsum}}{CaSO_4} \rightarrow \underset{\text{Partially soluble}}{Ca(HCO_3)_2} + \underset{\text{Soluble}}{Na_2SO_4} \downarrow \tag{6.34}$$

$$\underset{\text{Partially soluble}}{Ca(HCO_3)_2} \rightarrow \underset{\text{Insoluble}}{CaCO_3} \downarrow + H_2O + CO_2 \uparrow \tag{6.35}$$

If one leaches down these soluble salts prior to gypsum application, then most of the added soluble-Ca^{2+} can be used for replacing exchangeable-Na^{+} (Abrol and Dahiya 1974; Keren and Kaushansky 1981) and thus large quantities of amendments can be saved. In view of that, gypsum should be applied after the first irrigation, which will ensure maximum leaching of soluble CO_3^{2-} and HCO_3^{-} and make those unavailable for precipitating soluble-Ca^{2+} of the added gypsum. For the same reason, GR of soil should be determined after leaching the soluble salts.

6.5.4 *Quantity of Amendment Required*

While gypsum requirement (GR) is a chemical property of a given depth of soil and refers to the requirement of pure gypsum to reduce its ESP to less than 15, the quantity of amendment required (QGR) is an agronomical need of soil to reduce its ESP to a desired level depending upon the choice of crop to be raised (its sodicity tolerance, and rooting depth), CEC, depth of soil to be reclaimed, amount and nature of soluble salts, quality of available irrigation water, purity, and efficiency of the amendment to be used. A generalized equation (Eq. 6.36) for calculating QGR can be:

$$\begin{aligned}&\text{Quantity of gypsum required (QGR)}\\&\quad = [0.0086\ \text{F.Ds.}\rho\text{b.(CEC).}(\text{ESP}_1 - \text{ESP}_2)]\\&\qquad \times \text{purity of agricultural grade gypsum}\end{aligned} \tag{6.36}$$

Where

QGR = quantity of agricultural grade gypsum required, t ha^{-1},
F = $Na^{+} - Ca^{2+}$ exchange efficiency factor, unit less; Generally, it is taken as 1.20 (Richards 1954).
Ds = depth of soil, m,
ρb = bulk density of soil, kg m^{-3},
CEC = cation exchange capacity of soil, c mol kg^{-1},
ESP_1 = initial ESP of soil,
ESP_2 = final ESP required.
Ds.ρb represents the weight of soil, and
(CEC).($ESP_1 - ESP_2$) represents the amount of Na^{+} to be replaced.

Yadav and Agarwal (1959) reported that a dose that can reduce the ESP by 60–70% is an economic level of gypsum. Extensive work done at the Central Soil Salinity Research Institute, Karnal, India, have shown that 10–15 t of agricultural grade gypsum containing 70% $CaSO_4.2H_2O$, which approximates about half of the actual GR determined by Schoonover's method, is sufficient to reclaim surface 15 cm soil of one hectare, if one is to start with rice as the first crop (Table 6.37). This is keeping in view the high ESP-tolerance of rice, its shallow root system and capacity to solubilize soil $CaCO_3$ to further reduce ESP during its growth period.

Table 6.37 Yield, t ha^{-1}, of crops as affected by gypsum treatment in an alkali alluvial soil

Gypsum, t ha^{-1}	Sesbania 1970[a]	Wheat 1970–71	Rice 1971	Wheat 1971–72	Rice 1972	Wheat 1972–73	Mash 1973	Lentil 1973–74	Pearl millet 1974	Gram 1974–75
0	0.44	0.00	4.39	1.52	7.18	1.35	0.052	0.28	1.06	0.124
7.5	3.99	1.89	6.21	2.79	7.23	1.96	0.249	0.82	1.33	0.468
15.0	4.35	3.49	6.39	3.45	7.13	2.43	0.318	1.16	1.96	0.688
22.5	4.70	4.16	7.08	3.72	7.17	2.26	0.381	1.36	1.81	0.904
30.0	4.50	3.79	6.66	3.98	7.03	2.74	0.419	1.40	1.94	0.928
LSD at P = 0.05	0.51	0.64	0.81	0.70	NS	0.50	0.123	0.35	0.52	0.440
Normal yield[b]	10–20	4.50	7.00	4.50	7.00	4.50	1.000	2.00	3.00	2.000

Initial soil pH_2 = 10.3; ESP of surface 15 cm soil = 94
Source: Abrol and Bhumbla (1979)
[a]Green matter yield
[b]Normal yield refers to the yield in adjoining non-alkali soil

In general, it is observed that a dose of 2–20 t ha^{-1} gypsum for 0–15 cm soil is sufficient for raising rice and wheat crops in medium textured alkali alluvial soils. For reclaiming the upper 30 cm of soil, one may need about double of that amount. The quantity of gypsum can be reduced to half by additional application of FYM @10 t ha^{-1} and by adopting salt-tolerant shallow-rooted crops / varieties. Over time, the ESP of surface as well as of deeper layers gets reduced so as to allow cultivation of other crops. However, to grow sensitive crops like pulses and deep-rooted crops like cotton and mustard, one needs to add high amounts of amendments, 4 to 40 t ha^{-1}, right at the start of reclamation. Due to higher CEC, the amount of gypsum required is more for alkali Vertisols as compared to the alkali alluvial soils.

6.5.5 *Fineness of Amendment*

At the mine site, gypsum is obtained in the form of lumps which needs to be ground before application. Finer gypsum particles (Table 6.38) require less amount of water for their dissolution (Hira et al. 1981; Chawla and Abrol 1982) and react faster. But very fine gypsum particles are prone to wind-blown during application, and inactivation through precipitation of $CaCO_3$ on their surface. Moreover, the cost increases with increase in fineness of gypsum.

Khosla and Abrol (1972) suggested that gypsum of size finer than 0.59 mm (passed through 30 mesh sieve) would be more effective than coarse grade. Field and laboratory studies (Chawla and Abrol 1982) have shown that gypsum lumps when ground to pass through 2 mm sieve contain sufficient fine sized particles to effectively reclaim alkali soils. A mixture of fine and medium sized particles maintains a steady electrolyte concentration that is important for the maintenance of permeability of low salinity alkali soils. Increasing fineness of pyrites increases the specific surface area which promotes auto-oxidation of sulphur and results in higher water-soluble sulphur (SO_4^{2-}-S) thus increasing its efficiency. Singh et al. (1981) observed an increase in water-soluble S content with increase in fineness of pyrites (Fig. 6.8).

Table 6.38 Effect of particle size on the solubility of gypsum

Fineness of gypsum, mm	Amount of gypsum dissolved, g 100 ml^{-1}	Depth of water required, cm
< 0.10	2.00	2.50
< 0.26	1.43	3.50
< 0.50	1.05	4.75
0.26–0.50	0.59	8.50
0.50–2.00	0.42	12.00

Source: Hira et al. (1981)

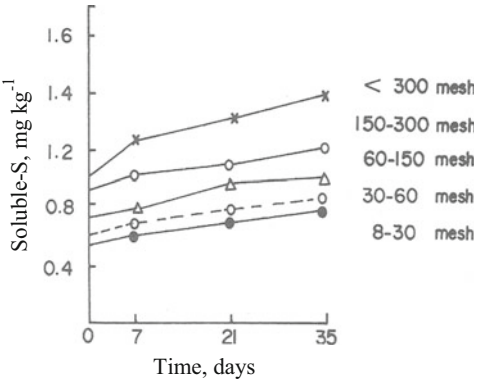

Fig. 6.8 Effect of particle size on the oxidation of pyrites (Singh et al. 1981)

6.6 Method of Gypsum Application

Amendments should be applied after proper bunding, land shaping and levelling of the field. Prior to gypsum application, a light irrigation should be given to ensure maximum leaching of soluble CO_3^{-2} and HCO_3^{-} so as to avoid immobilization of added gypsum through precipitation and thus to decrease its efficiency.

To ensure proper dissolution of gypsum and leaching of replaced Na^+, water is to be ponded on the soil. Normally, it takes 7–10 days to dissolve 70–80% of the added gypsum, bring down ESP to the desired level and to ensue leaching of reaction products. However, when rice is to be taken as the first crop, which is recommended, gypsum can be broadcasted in the standing water and seedlings transplanted without waiting for its complete dissolution. In such case, post-application leaching is also not needed and rice can be transplanted immediately after gypsum application. This is due to relatively high ESP-tolerance of rice. The water applied for growing paddy can itself be used for dissolving amendment and to leach down the reaction products from the effective rootzone. But when wheat, barley or any other upland crop is to be taken as the first crop, sufficient irrigations, 3–4 of 7.5 cm each, should be applied to dissolve gypsum, leach down the reaction products and to bring down soil ESP to a desirable level, before sowing.

When pyrites, elemental sulphur or by-product-S are used as amendments, then to maintain proper moisture and aerobic conditions, required for maximum oxidation and thus higher production of H_2SO_4, a cycle of wetting and drying should be adopted.

6.6.1 Depth of Mixing

Amendment should be broadcasted on the surface and then mixed in only shallow depths (upper 10 cm soil) to achieve better results. Field studies (Khosla et al. 1973)

have shown that mixing limited quantities of gypsum in deeper layers results in its dilution and higher inactivation by soluble salts resulting in low crop yields (Table 6.39). Singh et al. (1981) observed that mixing gypsum in surface few centimetres of soil is very effective and reduces expenditure on amendment application without scarifying yield of the first rice crop. El-Gabaly (1971) reported that gypsum mixed with surface 15 cm soil removed exchangeable-sodium more effectively than did gypsum applied to surface.

In alkali Vertisols where the amount of gypsum required for reclamation is high, and depth of reclamation in first year is limited to upper 20 cm soil layer, it is advisable to apply amendment only in the furrows (or strips) than broadcasting it on the entire surface of field. In addition to saving amendment, this enhances infiltration rate of the cropped area and depth of root penetration (Table 6.40) resulting in higher yield of upland crops like cotton (Gupta et al. 1993). Fertilizers are also applied to that reclaimed area for their better efficiency. The un-reclaimed area between the rows, being poor in infiltration, acts as catchment area to harvest rainwater for the crop raised in the reclaimed furrows (strips). However, under such situations, soluble Na^+-salts from the un-reclaimed areas between the furrows can re-sodicate the reclaimed area of strips, reducing the effectiveness of gypsum with time.

Table 6.39 Grain yield of crops as affected by quantity of gypsum and depth of mixing in an alkali alluvial soil

Amount of gypsum added, t ha^{-1}	Depth of mixing, cm	Grain yield, t ha^{-1}		
		Barley	Rice	Wheat
13.5	10	2.64	7.02	3.28
	20	2.46	6.05	3.16
	30	0.53	5.64	2.00
27.0	10	2.83	6.71	3.67
	20	3.22	6.28	3.67
	30	2.30	5.98	3.58

Source: Khosla et al. (1973)

Table 6.40 Effect of different modes of gypsum application on depth of root penetration and cotton yield in an alkali Vertisol

Treatments	Depth of root penetration, cm		Cotton yield, t ha^{-1}	
	First year	Second year	First year	Second year
Control	12.5	11.2	1.90	1.21
Mixing gypsum in the surface 20 cm soil layer	15.2	17.1	4.38	3.97
Mixing gypsum in set furrows of 60 x 30 cm	23.6	25.2	6.68	4.38
Mixing gypsum in set furrows of 60 x 15 cm	26.2	25.7	6.52	4.18
LSD at P = 0.05	–	–	1.99	0.84

Source: Gupta et al. (1993)

6.6.2 *Split Application of Gypsum*

Application of recommended amount of gypsum as a single dose, at the time of starting reclamation is superior to that of its application in two equal splits i.e. applying half of the required amount to each crop (Table 6.41). This is mainly due to effective decrease in pH / ESP of the soil to a threshold value of the first crop, brought about in the beginning itself. Results of field experiments showed that yield of rice and wheat, both in alkali alluvial and sodic Vertisol, were higher when the recommended amount of gypsum was added as a single dose rather than split in two doses (Gaul and Dargan 1978; Sharma et al. 1998).

Whole recommended dose of amendment should be applied in the beginning itself to ensure reduction of ESP to the desired level, commensurate with tolerance of the selected crop. It is not advisable to split the recommended dose of gypsum between two seasons or 2 years of reclamation. This slows down the rate of reclamation and results in lower yields of alkali-sensitive crops.

6.7 Removal of Salts and Reaction Products: Flushing *Vs* Leaching

Alkali soils have low infiltration rate and thus leaching or vertical removal of soluble salts, originally present in soil and the reaction products formed during reclamation, is a slow process. In fact, in highly dispersed alkali soils which often contain impermeable hardpans, it takes long time to leach down soluble salts by ponding water on surface. Due to this, sometimes an advice is given to flush-out salts, referred as horizontal leaching / removal of salts, by stirring the soil and draining the standing water. Qadir et al. (1998) observed that application of gypsum and flushing resulted

Table 6.41 Effect of split application of gypsum on grain yield, t ha^{-1}, of rice and wheat in an alkali alluvial loam and alkali Vertisol clay soil

Rates of gypsum, % GR, and its frequency of application	Alkali alluvial, loam soil			Alkali Vertisol, clay soil		
	Rice	Wheat	Total	Rice	Wheat	Total
Control	0.769	0.372	1.141	0.178	0.484	0.662
25	1.766	1.487	3.253	0.863	0.900	1.763
50	2.656	1.871	4.527	1.813	1.512	3.325
25 + 25[a]	2.493	1.535	4.028	1.130	1.169	2.299
75	2.537	2.269	4.806	2.584	2.309	4.893
25 + 50[a]	2.586	1.933	4.519	1.518	1.516	3.034
50 + 25[a]	2.693	2.137	4.830	2.055	1.889	3.944
25 + 25[a] + 25[a]	2.611	1.865	4.476	1.596	1.322	2.918
LSD at P = 0.5	0.570	0.401	–	0.924	0.388	–

Source: Sharma et al. (1998)
[a]Applied to the second crop

in better amelioration in soil salinity-sodicity and crop production. But this has the following draw backs:

(i) Horizontal flushing or drainage of the surface effluent poses problems of its disposal. One cannot drain out the salt-loaded effluent into neighbour's field or in the drain.
(ii) It increases the cost of reclamation as one needs to construct and maintain field drains and the main surface drain.
(iii) Along with soluble salts there is a risk of losses of dispersed clay particles, Ca^{2+} of the added gypsum and water-soluble K and P affecting soil fertility.
(iv) Flushing soluble salts from surface decreases the electrolyte concentration. This encourages soil dispersion, clogging of the surface pores and thus decreases infiltration rate, slowing the process of reclamation of subsoil.
(v) It increases (Irrigation) water needs of reclamation.

Hence, to hasten removal of soluble salts, it is not advised to flush the muddy standing surface water. Rather one should apply gypsum, improve chemical and physical properties of the surface soil and let soluble salts and the reaction products leach down vertically through the soil column, get redistributed in soil profile and ultimately join groundwater. During leaching, the soluble salts already present on surface, and the reaction product (Na_2SO_4) together with dissolved gypsum ($CaSO_4$) maintains the electrolyte concentration which discourages soil dispersion and thus prevents clogging of soil pores. Further, Na_2SO_4, the reaction product in the leachate, from surface layer (Eq. 6.37) reacts with native insoluble $CaCO_3$ in *situ* in subsoil layers forming secondary $CaSO_4$ (Eq. 6.38) which helps in lowering ESP of the subsoil. This decreases gypsum requirement of the whole profile and water requirement for leaching the reaction products. At the bottom-end of soil profile, one gets maximum amount of Na_2CO_3 followed by Na_2SO_4 in the leachate. This is also the reason, why pH and RSC of groundwater slightly increases in the initial years of reclamation.

$$\underset{\text{Alkali soil}}{2Na^{+}\text{-soil}} + \underset{\text{Applied gypsum}}{CaSO_4} \rightarrow \underset{\text{Good soil}}{Ca^{2+}\text{-soil}} + \underset{\text{Leached down to lower layers}}{Na_2SO_4 \downarrow} \tag{6.37}$$

$$\underset{\text{Reaction product from surface layer}}{Na_2SO_4} + \underset{\text{Native insoluble calcite}}{CaCO_3}$$

$$\rightarrow \underset{\text{Secondary gypsum formed insitu}}{CaSO_4} + \underset{\text{Sodium carbonate leached down to GW}}{Na_2CO_3 \downarrow} \tag{6.38}$$

6.8 Water Requirement for Dissolution of Gypsum

Dissolution of solid gypsum in water is represented as

$$\begin{aligned} CaSO_4.2H_2O\,(s) &\rightarrow CaSO_4(aq.) + 2H_2O \\ CaSO_4(aq.) &\leftrightarrow Ca^{2+} + {SO_4}^{2-} \end{aligned} \tag{6.39}$$

Solubility product of gypsum can be written as

$$\mathrm{Ksp} = \frac{\mathrm{a\ Ca^{2+}.a\ SO_4{}^{2-}}}{\mathrm{a\ CaSO_4}} \tag{6.40}$$

When added to alkali soils, soluble calcium replaces sodium on exchange complex according to the following equation:

$$\begin{aligned} &2\mathrm{Na^+(Exch.)} + \mathrm{Ca^{2+}(Solu.)} + \mathrm{SO_4{}^{2-}(Solu.)} \\ &= \mathrm{Ca^{2+}(Exch.)} + \mathrm{Na_2SO_4(Solu.)} \downarrow \end{aligned} \tag{6.41}$$

This reaction can be described by the thermodynamic equilibrium constant as

$$\mathrm{K_{Na}^{Ca}} = \frac{\mathrm{a\ Ca^{2+}(Exch.).\{a\ Na^+(Solu.)\}^2}}{\mathrm{\{a\ Na^+(Exch.)\}^2.a\ Ca^{2+}\ (Solu.)}} \tag{6.42}$$

Thermodynamic equilibrium constant K for the reaction can be written as

$$\mathrm{K} = \frac{\mathrm{a\ SO_4{}^{2-}(Solu.).a\ Na^+(Solu.)\}^2.a\ Ca^{2+}(Exch.)}}{\mathrm{a\ CaSO_4(Solu).\{a\ Na^+(Exch.)\}^2}} \tag{6.43}$$

This can be further rewritten as:

$$\mathrm{K = Ksp.K_{Na}^{Ca}} = \frac{\mathrm{a\ SO_4{}^{2-}(Solu.).\{a\ Na^+(Solu.)\}^2.a\ Ca^{2+}(Exch.)}}{\mathrm{a\ CaSO_4\ (Solu.)\}.\{a\ Na^+\ (Exch.)\}^2}} \tag{6.44}$$

This means that solubility of gypsum is equal to solubility product of gypsum in water times the thermodynamic equilibrium constant. It is apparent that the amount of gypsum dissolved will be more and thus amount of solid gypsum left will be less as the amount of exchangeable-Na^+ increases, meaning there by that gypsum solubility will be more in high ESP soils. This will further increase when the reaction product i.e. $SO_4{}^{2-}$ and Na^+ are continuously removed from the site as a result of leaching.

Gypsum solubility in alkali soils is also affected by:

(i) The size of gypsum particles, which affects its specific surface area and thus contact with water and solubility (Khosla and Abrol 1972; Kemper et al. 1975; Pal and Poonia 1979; Singh et al. 1981; Chawla and Abrol 1982).
(ii) The rate of Ca^{2+}-diffusion from the solution to the exchange sites and the rate of Na^+-diffusion away from the exchange sites i.e. $Na^+ - Ca^{2+}$ exchange efficiency (Dutt et al. 1972; Richards 1954).
(iii) SAR, ionic strength, ion pair association and C_{Mg}/C_{Ca} ratio (Tanji 1969; Oster 1982).

Soil exchange complex of alkali soils acts as a sink for Ca^{2+}, released from solid phase gypsum into soil solution; and as Ca^{2+} released by gypsum dissolution is used up in replacing exchangeable-Na^{+}, more of it is released from solid to the solution phase. The solid phase gypsum thus continues to dissolve till Ca^{2+} in solution phase is in equilibrium with the Na^{+}- Ca^{2+} of the exchange complex. Hence the same amount of water acts as a medium facilitating dissolution of gypsum from solid phase resulting in increase in amount of gypsum dissolved per unit amount of water (Chhabra 1996). Thus, the amount of gypsum dissolved per unit of applied water increases manifold when incorporated in alkali soils. This process continues till solution phase is saturated with Ca^{2+} i.e. the ion activity product of Ca^{2+} and SO_4^{2-} equals the solubility product of gypsum and this will happen only when most of the Na^{+} is replaced from the exchange complex.

However, irrigation water requirements during reclamation of alkali soils have often been exaggerated on the premise that solubility of gypsum is low and it would need large quantities of water to dissolve tonnes of applied gypsum. Solubility of gypsum in free water is 0.26% or 2.6 g L^{-1} at 25 °C. On this basis, the USDA Salinity Laboratory Staff (Richards 1954), recommended an application of 92–122 cm of water to dissolve 9–11.2 t ha^{-1} of agricultural grade gypsum of such fineness that 95% of the material will pass through a 100-mesh sieve. Dutt et al. (1972) observed that solubility of gypsum was affected by a mixture of salts in the soil solution and the Na^{+}- Ca^{2+} exchange equilibrium in the soil. Through a computer simulation model based on the solubility of gypsum and sodium exchange equation, Dutt (1964) and Dutt et al. (1972) predicted that 52–72 cm of water was required to dissolve 16.5–24.0 t ha^{-1} of applied gypsum.

Abrol et al. (1979) reported that in soil system, the quantity of gypsum dissolved increases linearly with increase in ESP of soil. At the highest ESP of 78.9, approximately 7.44 g gypsum dissolved per litre, which was nearly 3 times its solubility in pure water. They observed a significant relationship ($r = 0.98$) between mean per cent gypsum solubility (Y) and ESP of soil (X) described by the equation $Y = 0.0186\ X + 0.18$. Hira et al. (1981) found a linear relationship between exchangeable-Na^{+} and dissolution rate of gypsum of different sizes, ranging from 0.1 to 2.0 mm. That was described by the equation $Y = 0.46\ X + 2.1$, where Y and X are the gypsum solubility and gypsum requirement of soil, respectively.

Hira and Singh (1980) observed that 4 cm of water was required to dissolve the added gypsum (< 0.26 mm size) and to reclaim an alkali soil (Fig. 6.9). They further reported that the water required to dissolve gypsum did not increase if the amount of gypsum added was equal to gypsum requirement of soil. At higher gypsum requirement i.e. at high ESP, gypsum dissolution per unit amount of water increases significantly. However, a total of 26 cm of water i.e. about four irrigations, are required to leach down the reaction products in alkali soils. Arora et al. (1981) also reported higher dissolution of gypsum in alkali soils.

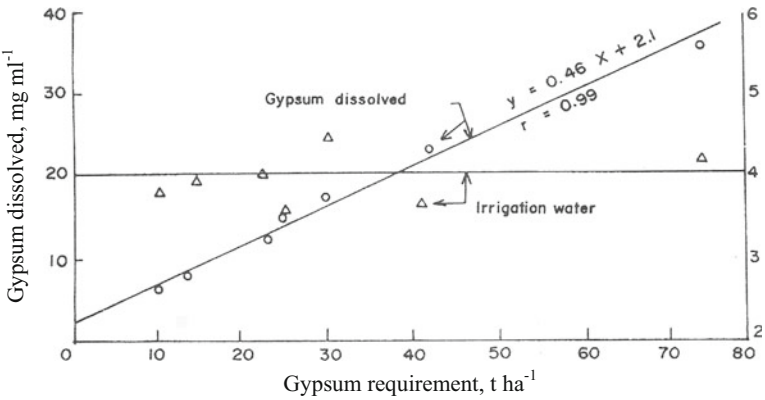

Fig. 6.9 Effect of gypsum requirement of soil on gypsum solubility and on irrigation water needs for gypsum dissolution (Hira and Singh 1980)

6.9 Role of Rice as a Reclamation Crop

Growing of rice, along with other cultural practices has been observed to enhance reclamation of alkali soils. Beneficial effect of rice (low-land paddy) cultivation can be attributed to the following reasons:

(i) Rice plant can tolerate and infect, likes standing water during its growth. This is a distinct advantage for crop growth in alkali soils. Other crops which cannot tolerate standing water and or poor air and water permeability do not perform well in these soils.

(ii) The water used for raising rice crop is simultaneously used for dissolving gypsum, leaching of salts and reaction products.

(iii) Transplanted rice crop can relatively tolerate higher degree of soil exchangeable-Na^+ and thus reclamation can be started even after application of less amount of amendment.

(iv) Chhabra and Abrol (1977) from controlled green house and laboratory studies observed higher production of HCO_3^- in the leachate at all levels of ESP, in the presence of than without rice plants (Fig. 6.10). They reported that due to submergence and biological activities of rice roots, pCO_2 increases and that results in higher solubility of soil-lime through its conversion into $Ca(HCO_3)_2$ (Eq. 6.45). Calcium of the solubilized $Ca(HCO_3)_2$ lowers ESP by replacing Na^+ from the exchange complex which in turn is leached out as $NaHCO_3$ (Fig. 6.11) as per Eq. 6.46. Significantly higher amounts of Na^+ were removed from

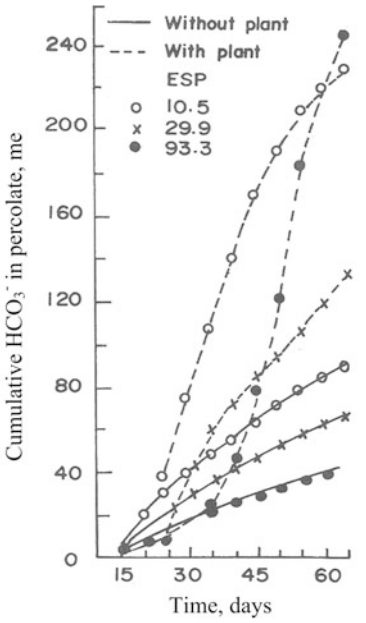

Fig. 6.10 Effect of rice growth on HCO_3^- content of the percolate from soils of different ESP (Chhabra and Abrol 1977)

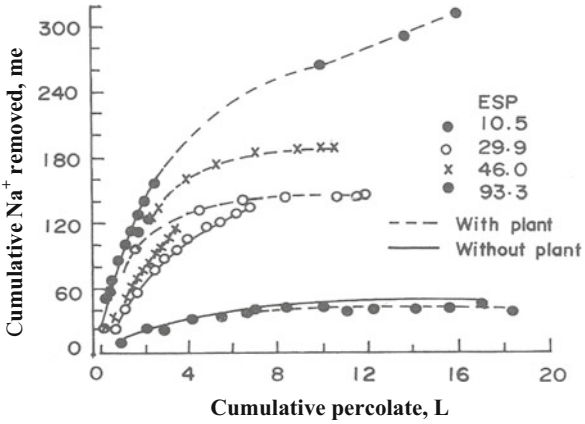

Fig. 6.11 Cumulative soil Na^+ removed as related to cumulative volume of the percolate in the presence of and without rice plant (Chhabra and Abrol 1977)

treatments with rice over the treatments without rice plant (Table 6.6) resulting in lowering of ESP and pH of soil.

$$\underset{\text{Insoluble, Present in soil}}{CaCO_3} + \underset{\text{Biological from rice roots}}{CO_2} + H_2O \rightarrow \underset{\text{Soluble}}{Ca(HCO_3)_2} \quad (6.45)$$

$$\underset{\text{Alkali soil}}{2Na^+\text{-soil}} + \underset{\text{Formed in situ}}{Ca(HCO_3)_2} \rightarrow \underset{\text{Reclaimed alkali soil}}{Ca^{2+}\text{-soil}} + \underset{\text{Soluble, to be leached down}}{2NaHCO_3 \downarrow} \quad (6.46)$$

Due to this, under field conditions, not only there was substantial decrease in $CaCO_3$ content of surface soil but the calcic layer present at a depth of 1 m also disapperared after 20 years of continuous rice-wheat cultivtion.

They further observed that, because of the activities of rice roots, pH of soil as indicated from pH of the percolate (Table 6.42), decreased sharply, which in turn increased solubility of native $CaCO_3$. Because of decrease in pH, dissolution of organic matter in soil decreased resulting in the leachate from treatments with rice becoming colorless. Thus leaching of alkali soils in the presence of rice plants also helps in conserving soil organic matter, losses of which otherwise are quite substantial in such soils.

(v) McNeal et al. (1966) observed that rice cultivation indirectly facilitates the removal of exchangeable-Na + by increasing the cross-sectional area of conducting pores, resulting in increased permeability. Chhabra and Abrol (1977) observed that in highly alkali soils, rice roots provide channels for the movement of water, which increases percolation rate and helps in leaching of salts and reaction products.

(vi) Growing rice in poorly drained alkali soils helps in storing 10–20 cm of rainwater right in the fields. This reduces the drainage needs of the area, minimizes the peak flow rates as well as helps in recharging the groundwater (Narayana 1979).

Due to these reasons, rice is not only an ideal crop for alkali soils but also enhances the reclamation process considerably. As a result of rice cultivation, ESP of not only surface but also of deeper layers decreases over a period of time (Fig. 6.12). Considering these, it is recommended that in first 4–6 years, rice crop

Table 6.42 pH of the percolate as affected by presence and absence of growing rice plant in soils of varying ESP

Soil ESP	Treatments	pH of the percolate, on days after transplanting		
		15	35	65
93.3	Without plant	9.48	9.33	8.72
	With plant	9.43	9.30	7.97
46.0	Without plant	8.68	8.62	8.00
	With plant	8.63	8.37	7.68
29.9	Without plant	8.23	8.08	7.65
	With plant	8.18	8.13	7.62
10.5	Without plant	8.00	7.93	7.57
	With plant	7.82	7.82	7.42

Source: Chhabra and Abrol (1977)

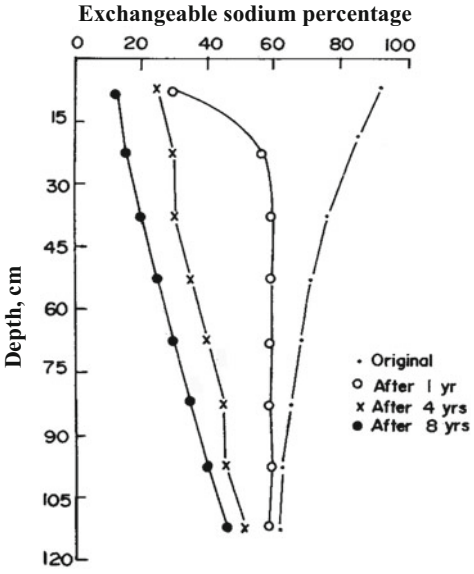

Fig. 6.12 Changes in soil ESP as a result of rice-wheat cropping in an alkali alluvial soil (Chhabra 1996)

should be included in cropping sequence to be followed in alkali soils. Rice-based cropping systems suitable for alkali soils are: rice – wheat; rice – barley; rice – Egyptian clover (berseem); rice – mustard, and sesbania (as green-manure) – rice – wheat. If it is done then other crops, which are sensitive to sodicity, can be grown profitably in reclaimed alkali soils after that period.

6.10 Geo-Hydrological Situations and Suitability of Soil for Rice Cultivation

Though rice is a highly suitable crop for poorly drained alkali soils under monsoon type of climate (Chhabra and Abrol 1977) and in coastal saline areas (Klein 1986), it should not be cultivated in dry-land areas with deep water table. It should also be not raised where high RSC-water is the only source of irrigation, a situation that will lead to deterioration of surface soil properties and poor permeability. Though it may not affect the rice crop itself, it will be detrimental to the following upland crops. The deleterious effect of high RSC, SAR-waters is more under rice-based cropping system than under cotton, maize and pearl millet in rotation with wheat. This is due to more number of irrigations and greater depth of water used in low-land rice than in upland crops. Rice yield in problem soils is affected by:

(i) The method of its cultivation i.e. direct sown through seeds *vs* transplanting seedlings.
(ii) Nutritional disorders due to low native fertility and or nutritional depletion or imbalance caused by intensive cultivation and injudicious fertilizer use.

Table 6.43 Geo-hydrological situations and suitability of soil for rice cultivation

Geo-hydrological situations	Type of soil	Suitability for growing rice crop
Shallow water table of good quality, poor drainage. Deep water table, groundwater of good quality, plenty of canal water, poor drainage.	Alkali soil Alkali soil	Most suitable Suitable
Deep water table, high RSC, enough canal water. Shallow water table with hardpan close to the surface, poor drainage.	Alkali soil Alkali soils	Suitable Suitable
Shallow brackish water table, no drainage, good quality canal water available. Deep water table, brackish, not enough canal water.	Waterlogged saline soils Inland saline soils	Suitable Unsuitable
Inundation due to tidal sea water, not enough fresh water but plenty of rains.	Coastal saline soils	Suitable
Shallow water table with pyritic layer.	Acid-sulphate saline soils	Suitable with special management only

Source: Chhabra (1996)

(iii) Adverse effects of high pH as in alkali soils, leading to toxic concentration of Na, Al, Si; and low pH as in acid-sulphate soils causing toxicities of Fe, Mn and Al.
(iv) K*ankar* and or clay layer close to the surface obstructing vertical root growth, salt leaching and drainage as in alkali soils.
(v) High salt contents leading to osmotic and nutritional stress as in saline soils.
(vi) vi)High organic matter with poor internal drainage causing accumulation of toxic ions and oxygen stress as in peat soils.
(vii) vii)High permeability as in light textured soils causing low water availability and nutritional-efficiency.
(viii) Problems associated with topography and location such as excessive water ponding, plant submergence, soil erosion and poor drainage.

Geo-hydrological situations and suitability of soil for rice cultivation are summarized in Table 6.43.

6.11 Cultural Practices for Reclamation and Cropping in Alluvial Alkali Soils

Integrating the principles involved in biological, agro-hydrological and chemical reclamation of alkali soils on sustainable basis, the following package of practices have been developed. These include, agro-technical measures like land development, bunding and levelling which help in better application of irrigation and increase water-use efficiency. Provision of irrigation, proper field preparation, application of amendments, leaching of salts and reaction products, cultural practices for

raising rice and wheat, green manuring, judicious use of fertilizers, proper water management including that of rainwater, and drainage are integral components of the reclamation technology.

6.11.1 On-Farm Development

For successful adoption of reclamation technology, the farms should be properly developed. The on-farm development activities include:

(a) Land shaping and levelling.
(b) Bunding of the area.
(c) Provisions for irrigation; and
(d) Drainage.

The whole area should be divided into a number of small blocks. To avoid major earthwork, each block should be divided into small fields and levelled within keeping each field as a unit. During land shaping, drastic shifting of surface soil should be avoided as it will expose the subsoil containing high amounts of $CaCO_3$, which can pose difficulties in reclamation, and cropping of the area. To ensure proper water management and uniform leaching of salts, the field should be levelled properly. Land levelling is best accomplished by a laser leveller (Fig. 6.13) when the soil is in *vattar* conditions. After land shaping and levelling, the fields should be divided into small parcels of 0.05–0.01 ha each. These plots should be irrigated to

Fig. 6.13 Laser land leveller for precision levelling of fields. (Photo: Chhabra)

locate lower and higher spots within the plots. Based on that, these should be levelled again for uniform spread of water and to prevent development of slick spots which are difficult to reclaim at the later stages and cause patchy growth of crop. Maximum slope of 0.1% to drain excess water has been found to be an optimum for alkali soils.

In soils which have a compact layer or hardpan in the subsoil to a depth of 0.5 m, subsoiling or deep tillage or chiselling at an interval of 0.5 m may be practiced to improve physical conditions. It loosens subsoil, improves soil permeability, promotes leaching of salts and vertical growth of roots. This should be done before application of amendment. However, its short-lived benefits in alkali soils (Cresswell and Kirkegaard 1995) and high cost, has restricted its large-scale adoption by the farmers.

Strong peripheral bunds should be made to prevent entry of salt-rich water from adjoining areas and thus avoid resodification of the reclaimed areas. Each block within the field should be provided with borders to apply water for leaching and irrigation; and to store rainwater in the fields so as to prevent its loss through surface runoff. Drainage of excess surface water may be needed during rainy season to prevent damage to young rice seedlings in summer and to upland crops like wheat and barley in winter. In areas where there are possibilities of heavy rains, as during monsoons, provision of surface drains may also be made. These should be then connected to farm pond, groundwater recharge structures and lastly to the local drain. This is to avoid stagnation of rainwater in the field but to conserve every drop of rainwater in the farm itself.

Provision of good quality irrigation water is a must for successful reclamation of alkali soils. For this, a shallow cavity tube well should be installed in the area or supply of canal water may be ensured.

6.11.2 Field Preparation

Due to high pH and ESP, tilth of alkali soils is very poor. It is necessary to cultivate soil at optimum moisture level so as to prepare fine seedbed and to avoid clod formation. Best results are achieved when soil is at *vattar* conditions i.e. depending upon texture, soil moisture should be between 10 and 18% on dry-weight basis.

For initial field preparation, soil should be tilled to a shallow depth. Experiments conducted by Kanwar and Bhumbla (1960) at Kamma Farm in Punjab, India showed that deep ploughing and subsoiling did not prove superior to shallow cultivation in increasing yield of rice and barley. Similarly, as these soils are highly dispersed one, there is no need to puddle before raising rice crop. However, after 3–6 years of reclamation when soil ESP goes down and soil becomes more permeable (Chhabra 2000), it becomes difficult to retain standing water in paddy fields. This results in decline in yield of lowland paddy. Under such situations it is recommended that conventional puddling should be done to cut down percolation losses during paddy cultivation. As a result of downward movement of dispersed clay and continuous cropping with rice - wheat, a hard claypan may form, especially in heavy textured

alkali soils. That may restrict root growth of wheat, mustard, cotton and okra, affecting their yields. It is recommended that in reclaimed alkali soils, subsoiling or chiselling should be practiced after every 3–5 years to prevent the formation of claypans and to encourage proper root growth.

6.11.3 Crop Selection

In the initial years of reclamation, adverse chemical and physical conditions of soil limit the choice of crops to be raised in alkali soils. Depending upon the degree of soil sodicity, choice of suitable crops can be made as per the list given in Table 6.3. In general, rice is favoured as a beginner crop as it can tolerate relatively high soil ESP, water stagnation and even enhances the reclamation process itself.

The major difference between the attempts made earlier in countries like the USA, Hungary and Russia, and those made at the Central Soil Salinity Research Institute, Karnal, India, is the choice of first crop raised during reclamation of alkali soils. Barley, an upland crop, due to its high tolerance to soil ESP was used in those countries while lowland transplanted rice which tolerates waterlogging, encourages solubilization of applied gypsum and dissolution of native lime, facilitates leaching of salts and reaction products, was chosen as first crop for reclamation in India.

In the initial years, rice-based crop rotations like rice – wheat, rice – barley and rice – berseem are most suitable than barley – oats – alfalfa. As the reclamation proceeds and ESP of surface as well as of lower layers decreases, crops like sunflower, cotton and mustard can be included in the cropping sequence. Legumes like pea, gram and cowpea, and crops like maize should be raised after 3–5 years of reclamation. For the selected crops, varieties with higher sodicity tolerance should be preferred.

6.11.4 Plant Population and Nursery Preparation

Due to formation of surface crust, germination percentage of seeded crops is often low in alkali soils. Plant population further decreases due to high rate of mortality especially during early stages of plant establishment and growth. This together with poor tillering can reduce yield. Crop stand in alkali soils can be improved by increasing seed rate, number of seedlings per hill, reducing planting distance and by changing the method of raising.

In case of rice, better plant population is achieved by increasing number of seedlings per hill from 2 to 4 (Dargan 1979; Prasad et al. 1992), reducing planting distance from 20 × 20 (25 hills m^{-2}) to 15 × 15 cm (33 hills m^{-2}) or 15 × 20 cm (45 hills m^{-2}), and by gap filling so as to replace dead plants. For optimum yield, one should aim at 100 productive tillers per m^2. Depending upon the seed weight (which itself depends upon the grain-size and variety) and considering that in the initial

years, 3–4 seedlings / hill are to be transplanted; one will need about 40 kg of paddy seed for raising nursery for one hectare of alkali soil against 20 kg seed for raising nursery for transplanting in non-alkali soils. This is based on the assumption that 1000 seeds of most of coarse varieties weigh about 30 g and have 80% germination. The nursery should be raised on normal non-alkali soil on raised seedbeds (2 m × 10 m). Seeds should be sown by the end of May so that seedlings are ready for transplanting by the end of June. Before seeding, seedbeds should be supplied with well rotten FYM @ 50 kg, urea @ 2 kg, DAP @ 1 kg, MOP @ 1 kg and $ZnSO_4$ @ 0.5 kg per 100 m^2. Seeds should be treated against fungal infection and soaked from 12 to 18 h before broadcasting on nursery beds. During this process, half-filled and unfilled grains, floating on surface of water should be removed. Sprouted seeds should be broadcasted on soil in the standing water. Considering high temperatures during this period, nursery should be irrigated in the evening and higher depth of standing water should be avoided during the day. Weeding and proper plant protection measure should be taken to raise healthy seedlings. Before uprooting nursery, seed beds should be well irrigated so as to make the soil soft and thus avoid root damage. This also helps in avoiding entrance of salts through the broken and damaged roots.

In case of wheat, a seed rate of 100–125 kg ha^{-1} should be adopted. For late-sown varieties, seed rate should be further increased by 25% over the recommended amount. In case of pearl millet, seed rate should be increased keeping in view the method adopted for sowing the crop. It should be 3–3.5 kg for dibbling method, 5–6 kg for drilling method and 6–7 kg for broadcasting method. Since tillering in the initial years of reclamation is low, plant spacing should be reduced from 45 × 15 cm to 40 × 10 cm so as to achieve optimum number of productive tillers. In addition to increasing seed rate and reducing planting distance, gap filling should be done by transplanting young seedlings at places where seeds have failed to germinate.

6.11.5 Age of Seedlings

Generally, sodicity tolerance of crop increases with age. For rice, older seedlings (40–45 days) have been found to establish better than younger seedlings (25–30 days) (Dargan and Gaul 1975; Dargan 1979; Prasad et al. 1992). In case of vegetables also, survival of older seedlings is higher as compared to younger seedlings. Similarly, for establishing tree species in alkali soils, planting older seedlings have proved to be more beneficial (Chhabra 1996).

In first 2 years of reclamation, there is a possibility of excess algal growth which can cover a large surface of rice fields. This can be of green, blue, brown or red colour depending upon the light intensity and temperature of the area. Though blue green algae, also called Cyanobacteria, a group of photosynthetic bacteria, due to its capacity to fix atmospheric-N_2, is beneficial to rice paddies yet its vigorous growth may restrict oxygen exchange between soil and atmospheric air and affect growth of young plants. In case of rice - fish culture, it may adversely affect survival and

growth of fishes. In paddies, its excessive growth can be prevented by minimizing the depth of standing water. However, care should be taken to keep soil moisture to near saturation.

6.11.6 Green Manuring

Application of green manure enhances OM, increases pCO_2 in soil solution, lowers pH, enhances solubility of native $CaCO_3$ and adds considerable amount of nitrogen in soil. pH of calcareous paddy soils is controlled by the chemical equilibrium of $CaCO_3$–CO_2 system and decreases due to accumulation of CO_2 during submergence. Applying green-manure to such soils can further lower pH by as much as 0.5–1.0 units as compared to that in no-green-manure plots. This benefits the growing crop and enhances yields. Green manuring with *Sesbania* has been found a very useful practice for reclaiming and maintaining fertility of alkali soils (Agarwal et al. 1950; Uppal 1955; Dhawan et al. 1958; Yadav and Agarwal 1961; Kanwar et al. 1965).

Sesbania (*Sesbania aculeate*) has proved to be an ideal green-manure crop for alkali soils because:

(i) It has relatively high tolerance to soil sodicity.
(ii) It is tolerant to short-term water stagnation, surface waterlogging.
(iii) It has narrow C:N ratio and thus decomposes very fast.
(iv) It produces high amounts of organic acids under high moisture conditions and thus helps in dissolving native $CaCO_3$.
(v) Since it grows during summer months (May–June), when there is no other crop in the fields, it fits into the cropping pattern to be followed in alkali soils.
(vi) It is a good cover crop during summer months and prevents upward movement (rising) of salts and thus avoids resodification of surface layers. Rather, due to irrigation during this period, it helps in pushing the replaced Na^+ to deeper layers.
(vii) It supplies 60–80 kg N ha^{-1} to soil and helps in mobilizing micronutrients like Fe, Mn and zinc.
(viii) Since it has well-developed roots, it opens up the soil and improves soil physical properties.

Depending upon the season and local conditions, several other plants (Table 6.44) can also be used for green manuring. Normally, 45 days old *Sesbania*, which attains a height of 1.5–1.8 m, is ideal for incorporation as green-manure. Longer growth-period renders the plants hardy and difficult to decompose. Being succulent and with a narrow C:N ratio (about 25), it decomposes very easily and quickly. Prior to sowing of main crops, green–manures are normally allowed to decompose for 10–15 days after incorporation in soil. Such a practice has been found to be inefficient in alkali soils, as due to high pH, it leads to loss of released ammonia by volatilization. Transplanting of rice seedlings, directly after incorporation of

Table 6.44 Green matter yield and % N content of common crops suitable for green manuring

Common name	Botanical name	Growing season	Green -manure yield, t ha^{-1}	N, % on fresh wt. basis
Sunn hemp, Indian hemp	*Crotalaria juncea*	Summer	21.2	0.43
Dhaincha, *Sesbania*	*Sesbania aculeata*	Summer	20.0	0.43
Pillipesera, African gram, black gram	*Phaseolus trilobus*	Summer	18.3	1.10
Mung bean, green gram	*Phaseolus aureus*	Summer	8.0	0.53
Cowpea Mugwan	*Vigna sinensis* *Vigna trilobata*	Summer	15.0 15.0	0.40 0.50
Guar, cluster bean	*Cyamopsis Tetragonoloba*	Summer	20.0	0.34
Senji, sweet clover	*Melilotus indicus* *Melilotus albus*	Winter	28.6	0.57
Khesari, chickpea	*Lathyrus sativus*	Winter	12.8	0.54
Berseem, Egyptian clover	*Trifolium alexandrinum*	Winter	15.5	0.43

green-manure and flooding the fields leads to better yields and N-recovery (Ghai et al. 1988). Standing water in rice fields hastens the decay of succulent green-manure crop without any harm to rice crop. A growth period of 45 days for S*esbania* and "no decomposition period" also results in saving of 10–15 days for cultivation of rice crop.

Since, about 50% of organic nitrogen content of green-manure crop is converted into readily available ammoniacal form within 4–6 days and the rest within 10–20 days of incorporation (under temperature conditions prevailing in the main rice growing season), it helps in meeting the initial needs as well as ensures steady supply of N during later stages of crop growth. It has been observed that increase in rice yield due to green manuring can be equivalent to about 80 kg of N applied through chemical fertilizers.

Application of green-manure, due to its priming effect on soil microbes, also increases the availability of soil nutrients like phosphorus and sulphur. Beneficial effect of green-manure is more when it is decomposed under anaerobic (saturated) conditions (Singh 1974). Gale and Gilmour (1988) reported a significant increase in per cent N mineralization under anaerobic as compared to under aerobic decomposition of alfalfa (Table 6.45)**.**

Application of green-manure results in better soil aggregation which may be the possible reason for decreased bulk density (Mishra and Sharma 1997). Kumar and Prasad (2008) studied the effect of continuous application of green-manure and concluded that it improves soil physical properties like bulk density, infiltration

Table 6.45 Effect of mineralization from alfalfa (3.24% N) under aerobic and anaerobic conditions

Treatments	Net N mineralized at different days, %				
	2	**7**	**14**	**22**	**30**
Aerobic	8.0	10.5	12.3	23.6	27.8
Anaerobic	11.7	26.5	43.2	40.7	38.9

Source: Gale and Gilmour (1988)

rate and size of water-stable aggregates. Application of organic matter in the form of crop residues also affects soil buffering capacity and moderates extreme temperature variations in the rootzone. Increase in organic matter through the use of FYM, compost, green-manure, crop residues etc. also buffers soil against changes in pH under use of high SAR, RSC-waters. Though these changes may be small yet prove significant for establishment of plants under hostile environments.

However, in spite of many advantages and extension activities to popularize this practice, most of the farmers are not adopting green-manure as a routine practice due to the following limitations:

(i) It needs pre-planning and proper time schedule to grow green-manure crop.
(ii) In intensive agriculture, farmers do not wish to set apart 6–8 weeks exclusively for growing a green-manure crop with no direct economic benefit. Except in case of mungbean (*Vigna radiata*) and cowpea (*Vigna unguiculata*) crop, there is no immediate economic gain to the farmers.
(iii) When green-manure crop is raised after harvest of wheat crop, farmers find it extremely difficult to do farm operations in the intense heat of May and June.
(iv) Non-availability of good quality water for raising green-manure crop poses restriction in water-scarce areas.
(v) Availability of good seeds of green-manure crops is a wide-spread problem.
(vi) Farmers are unable to appreciate benefits of green-manure since the benefits sometimes are not as spectacular as those observed from direct application of inorganic fertilizers.

6.11.7 Continuous Cropping

Alkali soils once reclaimed should be continuously cropped to keep the downward movement of replaced Na^+ and soluble salts. Leaving land without crop i.e. fallowing, encourages upward flux of salts and reverses the process of reclamation. Due to application of amendment, leaching and cultivation of lowland rice, there is a continuous reduction in ESP throughout the soil profile. This process can be further hastened by including crops like berseem and other green fodders which require frequent irrigations (Chhabra et al. 1988).

6.11.8 Nutrient Management

High exchangeable-Na^+, high pH, $CaCO_3$ content and high concentration of soluble CO_3^{2-} and HCO_3^- of alkali soils, adversely affect transformation and availability of several essential plant nutrients. Almost all crops grown in alkali soils, respond both to application of different fertilizer nutrients and to methods of their application. In general, alkali soils are deficient in Ca, N and Zn (Chhabra and Abrol 1983; Singh and Chhabra 1990; Singh et al. 1992; Chhabra 1996). A detailed discussion on nutrient management and principles of fertilizer application in salt-affected soils has been presented in Chap. 7.

6.12 Water Management

6.12.1 Rainwater Management

Considering poor permeability of alkali soils and lowland rice being the major crop raised during rainy season, the following three-tire system of rainwater management in cultivated alkali soils has been suggested by Dhruva Narayana (1979, 1980).

(a) Maximum amount of rainwater is to be collected and stored in the rice field itself till such time and extent as will not harm the crop. It has been observed that rainwater up to 15 cm storm during rainy season (a period of water abundance) can be stored in bunded rice fields especially after the initial 1 month of growth which also coincides with the period of maximum rainfall. By this way, one can store as much as 15–20 cm of rainwater per hectare. However, during early growth periods, care should be taken that the young plants do not get submerged in stored rainwater. This stored rainwater will meet irrigation needs of rice crop as well as help in dissolution of added gypsum and leaching of reaction products.
(b) Any excess water after its storage in crop-land should be stored in dug-out ponds located in the lower region of farm. This water can be recycled for irrigation during dry spells and off-rainy periods and thus helps in lowering the demand on groundwater and / or canal water. The stored pond water can also be used for freshwater fish culture and to recharge groundwater.
(c) The remaining excess rainwater is diverted into local drains and natural river system.

By adopting the above system, 80–90% of rainfall can be utilized and or stored within the farm and local areas. The peak runoff potential of alkali lands can be considerably reduced by agroforestry / silvipastoral practices (Kamra et al. 1986).

6.12.2 Drainage

Due to low infiltration rate of alkali soils, rainwater accumulates to create surface waterlogging. Even a low intensity shower or a normal irrigation may create temporary waterlogging and anaerobic conditions. Due to this, upland crops suffer due to excess moisture and oxygen-stress in alkali soils. To avoid this, provision of surface drainage, especially during the rainy season is a must for successful cropping in these soils.

In initial stages of reclamation, rainwater in the form of surface runoff contains high amounts of suspended clay and silt particles and high concentration of soluble Na_2CO_3 and $NaHCO_3$. It should not be allowed to pass on to the adjacent fields otherwise this can cause sodification of the good quality lands. It should be drained through a suitable outlet or retained within the field, by providing strong bunds, so as to seep down to lower layers. After first few rain-showers, quality of surface runoff is generally good. Instead of letting it go waste and contribute to floodwaters, it may be stored in shallow dug-out ponds on the farm itself.

In situations, where water table is high, which is mostly due to perched water table, and rainwater cannot percolate, then drainage is to be installed to avoid surface waterlogging. However, due to low hydraulic conductivity, conventional subsurface drainage to lower the water table is neither possible nor required in these soils (Pandey et al. 1975; Dhruva Narayana et al. 1977; Dhruva Narayana 1980). Normally, groundwater in alkali soils is of good quality and can be exploited for irrigation. For this a number of shallow cavity tube wells should be installed to act both as a source of irrigation and to provide vertical drainage. This has proved to be the most effective and economical way of controlling rise in water table and providing an assured source of irrigation for crop production (Tyagi et al. 1980).

Due to poor hydraulic conductivity of these soils, natural recharge of groundwater even during rainy season is minimum. While as a result of vertical drainage, through shallow tube wells, the decline in water table is relatively very fast. Sometimes, it even necessitates digging of pits to install motor of the centrifugal pump at deeper depths for obtaining an effective water discharge. This costs money and also exposes the farmers to hazards of poisonous gases which may accumulate in such dug-out pit-wells (Chhabra 1988a, b). To boost groundwater recharge, vertical bores with recharge shaft and or recharge cavity and appropriate filters may be provided (Kamra and Sharma 2011; Kamra 2013; Bhaskar et al. 2014). This will also minimize peak runoff and conserve rainwater right in the area.

6.12.3 Water Availability and Irrigation

Irrigation management in alkali soils poses peculiar problems due to clogging action of dispersed soil particles and low stability of soil aggregates, which limit water and air permeability of these soils. Because of this restricted entry from the surface,

enough recharge of the depleted soil moisture does not take place even during irrigation of alkali soils. Many times, it is observed that while the top soil may be wet but few centimetres below, it may be completely dry. Further, the amount of available water held by soil as defined by the moisture content between field capacity i.e. 0.1 bar, to wilting point i.e. −15 bars suction, is significantly reduced with increasing ESP (Abrol and Acharya 1975; Sandhu et al. 1980).

In addition to the above, during post-irrigation period, water transmission from lower layers to upper layers, to meet evapo-transpiration need of crops, is severely restricted due to low internal hydraulic conductivity of alkali soils. Acharya et al. (1979) observed that with increase in ESP of surface soil, water uptake by *Brassica juncea* was reduced drastically (Table 6.46). Not only that, contributions of sub-surface layers to water availability were low, practically none when ESP was high. Thus, for the same amount of total water content, the available water is much less in alkali soils as compared to that in normal soils (Fig. 6.14, Chhabra 1996).

Since, in early stages of reclamation only the upper soil layers are improved, bulk of plant roots are confined to only surface 30 cm depth. Thus, in addition to the limitations imposed due to adverse physical properties of alkali soils, limited root growth of plants further restricts the depth of soil explored for moisture extraction.

Table 6.46 Water extraction by *Brassica juncea* from different depths as affected by ESP of the surface soil

	ESP of surface 15 cm soil				
Water extraction	**4**	**11**	**16**	**23**	**38**
Extraction rate, cm day^{-1}	0.23	0.24	0.20	0.18	0.14
0–15	46.4	40.0	67.5	75.0	78.0
15–30	30.0	31.1	28.0	25.0	22.4
30–45	16.3	18.7	4.5	0	0
45–60	7.3	6.2	0	0	0

Mean of 17 days extraction period
Source: Acharya et al. (1979)

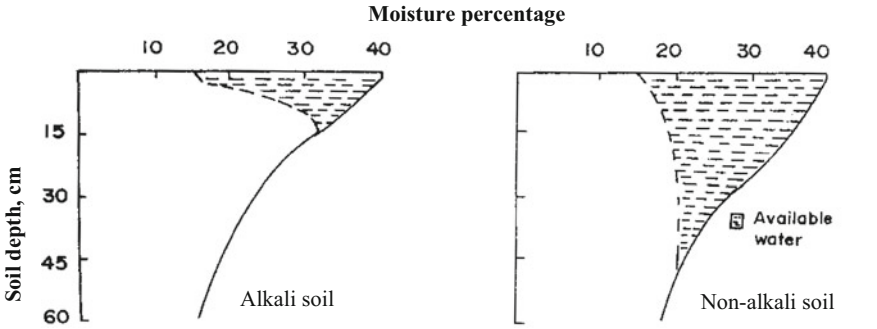

Fig. 6.14 Schematic diagram showing the amount of available water in a normal and an alkali soil (Chhabra 1996)

All these constraints affect ability of alkali soils to supply adequate amount of water to the growing plants.

As depth of irrigation water and interval between two irrigations depends upon evapo-transpiration (ET), nature of plant response to soil water stress, depth of roots; water storage and transmission characteristics of soil, it is found that light but frequent irrigations should be applied in alkali soils. Heavy irrigations which will supply water in excess of what can be absorbed by soil in few hours can result in temporary waterlogging and oxygen stress in the rootzone, affecting crop growth/yield. This means that total amount of irrigation water remaining the same, it should be supplied in small quantities but more frequently. Generally, 4–6 irrigations of 5 cm each will be required for wheat crop. To facilitate this, large fields should be divided into small irrigation blocks.

Normally, surface methods of irrigation like furrows, border strips or level basins are used for irrigating alkali soils. However, keeping in view their susceptibility to surface waterlogging, sprinkler method because of its ability to supply water uniformly and in regulated quantities is a better option. For trees and fruit plants, drip method is very successful and economical.

6.13 Yield Potential of Upland Crops in Reclaimed Alkali Soils

In general, rice yields in reclaimed alkali soils are more or equal to those in adjoining non-alkali fields. But even after many years of reclamation, the maximum yield of upland crops like wheat, barley, pearl millet and mustard etc. continues to be low in reclaimed alkali soils than in adjoining non-alkali soils. This is due to the following reasons:

(i) *Poor physical properties*: After reclamation through gypsum application and continuous cultivation, surface soil pH comes down to around 8.5, ESP < 15 and EC < 4 dS m^{-1} within 2–3 years i.e. the rate of improvement in chemical properties is faster and these become almost similar to those of the adjoining non-alkali soils. But the rate of improvement in physical properties like bulk density, soil aggregation, water retention and transmission, dispersion and hydraulic conductivity is slow (Chhabra and Khajanchi Lal 2007), which become a limiting factor in realizing high yields of upland crops under high-input agriculture. Amelioration in physical properties of alkali soils requires improvement not only in macro-porosity (pores with dia. Larger than 75 μm) which is associated with sol structure but also improvement in micro-porosity (pores with diameters between 5 and 30 μm) which is associated with pore space controlling capillary movement of water, air diffusivity, gaseous exchange and respiration within the rhizosphere; which is a slow process. Due to low amount of OM and poor biological activities, improvement in physical properties, especially of subsoil is much slower as compared to the rate of improvement

in soil chemical properties. Bulk density of reclaimed alkali soils increases with depth and is highest at 15–20 cm (mean 1.718 g cm^{-3}) showing that in these soils under rice - wheat cultivation, a hardpan is formed at that depth, which may restrict the downward movement of salts and growth of roots affecting yields of upland crops (Chhabra and Khajanchi Lal, 2007).

Further, once waterlogged due to surface water stagnation, alkali soils continue to suffer low redox potential and high oxygen-stress due to low internal drainage and poor physical properties. As a result of these, upland crops grown on reclaimed alkali soils suffer more due to poor aeration and yield less than the adjoining non-alkali soils.

(ii) *Low clay and silt content of surface layers*: In the beginning, both alkali and adjoining non-alkali soils have the same texture because both have the same parent material. But in alkali soils, during the process of sodification, clay and silt particles get dispersed and through the process of eluviation move from surface to lower layers. As a result of that clay and silt content of surface layers of alkali soils decreases and that of subsurface layers increases. Since, clay and silt particles are the storehouses of plant nutrients, the total nutrient content of surface layers decreases during the process of sodification. As this process is irreversible i.e. the clay particles once migrated to lower layers cannot come to the surface layer due to reclamation, total nutrient content of surface layers, the area which supports active roots of plants, remains low in reclaimed alkali soils than in the adjoining non-alkali soils. This is one of the major reasons why yields of upland crops in reclaimed alkali soils are lower than in the adjoining non-alkali fields.

6.14 Post-Reclamation Measures for Sustainable Management of Alkali Soils

Post-reclamation management of alkali soils is as important as reclamation process itself. Post-reclamation management of alkali soils is more difficult than that of saline soils**.** To maintain their productivity and health, there should be regular monitoring of such soils. The following steps may help in maintaining their productivity and prevent resodification:

6.14.1 Resodification of Reclaimed Alkali Soils and Repeat Application of Amendments

Alkali soils, once reclaimed remain productive and do not need repeated application of amendments provided these are continuously cropped. This is due to the fact that these soils contain appreciable amounts of $CaCO_3$, which together with Ca added through fertilizers like calcium ammonium nitrate, single super phosphate and

irrigation water is sufficient to meet calcium needs of plants and to keep Na^+ out of the exchange complex.

However, during initial years of reclamation, depending upon the amount of water that passes through the rootzone and internal drainage of soil, the leached salts and reaction products reside at different depths within the profile. Due to poor crop and water management practices, these leached salts and reaction products can return or rise to surface and resodify the reclaimed lands. These factors along with release of salts through weathering of soil minerals, change in climatic conditions (decrease in rainfall, increase in drought periods, high temperatures leading to high ET etc.), and subsurface intrusion of salts from neighbouring lands or groundwaters in the system may result in increased ESP forcing farmers to repeat application of gypsum in the previously reclaimed alkali soils.

In addition to these, the following situations can result in resodification of the reclaimed soils and decrease their productivity (Chhabra 1996):

(i) When farmers do not apply recommended doses of gypsum to start reclamation. This causes incomplete reclamation and poor leaching of soluble salts and reaction products from the effective rootzone, which may return to the surface and cause resodification. Low doses of gypsum also result in low Ca^{2+}-saturation [(Exchangeable Ca^{2+}/CEC) $\times$ 100] of soil exchange complex which affects Ca-availability to plants.
(ii) When large amounts of soluble sodium salts are added from outside, through flood waters from the adjoining un-reclaimed alkali fields.
(iii) When irrigation water has a problem of high RSC.
(iv) When there exists a shallow water table with high RSC, SAR and or high EC.
(v) When the area experiences prolonged dry fallow periods causing precipitation of soluble-Ca^{2+}.
(vi) When there is a change from high-water requiring to low-water requiring crops resulting in poor leaching and upward flux of reaction products.

Under above situations, previously reclaimed alkali soils may need repeated application of amendments to maintain and restore their health (Chhabra 1996; Chhabra and Kamra 2002). Farmers should take effective steps to prevent accumulation of soluble salts and reaction products so as to prevent resodification and avoid burden of repeat application of amendments. Regular monitoring of chemical and fertility status and quality of groundwater used for irrigation should form important component of strategy for post-reclamation management of alkali soils on sustainable basis. Updating of soil health cards should be a must for such areas.

6.14.2 Proper and Balance Use of Fertilizers

Fertility management of alkali soils is important not only in the initial years of reclamation and cropping but also in the later stages. It has been commonly observed that after 3–4 years of reclamation and continuous harvest of good crops, the farmers

complain of stagnation in yield, decline in yield levels and or poor efficiency of added fertilizers and conclude that the soil has deteriorated again. Such a situation should be carefully analysed with respect to the following points:

(i) *Imbalance use of nutrients*: In view of the specific needs of alkali soils, general application of multi-nutrient fertilizers such as NPK-mixtures with different grades; compound fertilizers like di-ammonium phosphate, nitrophos, mono-ammonium phosphate (MAP, $NH_4.H_2PO_4$, 11% N and 52% P_2O_5) and fortified fertilizers like zincated superphosphate (0.5% Zn, 16% P_2O_5), boronated superphosphate (Borophos with 16% P_2O_5 and 0.18% B) and boronated DAP, may not always be necessary in the initial years of reclamation. Avoiding their use saves money and minimizes the cost of reclamation (Chhabra 1988b). However, after 3–4 years of reclamation and intensive cropping, these soils need application of complex and multi-nutrient fertilizers to maintain soil fertility and sustain yields. One should realize that alkali soils after reclamation behave like "**alkaline calcareous soils**" which have low available nutrients and problem of lime-induced micronutrient deficiencies. Most commonly, farmers use high amounts of N and low amounts or no P and K even in the intensively cropped non-alkali irrigated areas. This has led to serious imbalance of nutrients in soil as a result of which the fertilizer-use efficiency goes down and yields are seriously affected. Not only yields but quality (nutrient content of grain, straw, vegetable and fruits; colour of grain etc.) and uniform maturity is badly affected causing concern about their marketability and food value.

(ii) *Decrease in soil fertility due to crop removal*: Initially the *barren* alkali soils may have enough native nutrients like K and P to supplement the levels of nutrients being added from outside to meet crop needs. But, over the years, with increase in yield levels there is higher removal of nutrients by crops. With continuous cropping and inadequate inputs (through chemical fertilizers, organic manures and crop residues etc.), fertility status of surface as well as subsurface soil decreases affecting yields. To correct this, doses of inorganic fertilizers have to be increased together with adoption of practices like application of FYM, green manuring and proper crop residue management etc. to maintain soil fertility so as to sustain crop production.

(iii) *Mismatch between fertilizer application and nutrient need of the crop*: After few years of reclamation, the farmers change the cropping sequence from rice - wheat to other crops like mustard, legumes, cotton and vegetables whose fertilizer needs may be different than those applied by the farmers. Different crops, crop rotations, cropping systems, mine plant nutrients in different amounts, proportions and from different soil depths. In such cases the type of fertilizers and the nutrient levels being used should be rescheduled to suit need of the crops.

6.14.3 Application of FYM and Green Manure

Alkali soils are poor in soil organic matter. In general, these soils contain <0.5% OM (Chhabra 1996). Though on cropping such soils, there is addition of OM through crop roots, leaf fall and left-over crop residues etc., these are not enough to raise it to the optimum levels. OM has a beneficial role in improving soil physical, chemical and biological properties together referred as soil health. It acts as a buffer, improves retention of nutrients, prevents their leaching losses, directly adds macro and micronutrients and increases their availability through complex formation, chelation and recycling. Due to its low levels, efficiency of applied inorganic nutrients gets truncated and this results in decreased crop yields with time. Loveland and Webb (2003) have suggested a critical level of 2% soil organic carbon (SOC, approximately 3.4% of soil OM) for maintaining soil productivity in temperate regions. But because of its rapid decomposition, it is not possible to build such a high amount of OM in soils of tropical regions. Aune and Lal (1997) and Lal (2006) have suggested a critical level of 1.1% SOC for soils of tropics, below which the yields will decrease by about 20%.

Due to the fact that (i) rice-based cropping is the major crop rotation and legumes except berseem are seldom included in crop rotation, (ii) crop residues (straw and stubbles) left after the harvest are removed for cattle feed or burnt in the field, and (iii) the farmers adopt crop-based rather than agroforestry-based system, there is no substantial build-up of OM in reclaimed alkali soils resulting in decrease in their quality and productivity.

Cultivation of reclaimed alkali soils without addition of OM amounts to "extractive practices" and deteriorates their quality. This deterioration over the time is exhibited in terms of decreasing crop yields and low efficiency of added inorganic fertilizers. To maintain soil health, availability of nutrients, productivity and sustainable use of reclaimed alkali soils, addition of OM through regular application of FYM, green-manure, vermicompost, press mud, better management of crop residues, inclusion of leguminous plants in crop rotation and use of agroforestry system is a must and should make a part of standard agronomic practices for their post-reclamation management.

6.14.4 Timely Sowing of Crops

Due to sudden rise in temperature at grain-filling and ripening stage, crop dries up and grain which is at the milking stage does not get sufficient time to develop fully, resulting in shrinking of its size and partial filling of ear-heads. This phenomenon known as "terminal temperature effect" or "**terminal heat stress**" results in decreased test-weight, lower yields and poor quality. Thus, in spite of good vegeta-

tive growth, grain yield decreases resulting in low harvesting index. This type of damage is more to late sown varieties of wheat and barley whose maturity time coincides with the onset of summer. In India, it is called "*HAVA NIKAL GAI*" and refers to blowing of strong heat waves near the stage of maturity affecting grain yield. Similar phenomenon happens to *Rabi* corn where along with decreased size, grain-filling of cob is severely affected due to sudden rise in temperature. During this period, the soil dries up and farmers are forced to give extra irrigation which causes lodging of crop, further reducing yield. In case of rice also, very high temperatures (> 35 °C) near maturity, induce heat stress and affect plant physiological processes, leading to spikelet sterility, non-viable pollens and reduced grain quality. Sometimes near maturity, there is sudden decrease in temperature which affects pollination and seed-setting, affecting crop yields. Hence it is important to sow crops timely and avoid damage due to sudden changes in climate at maturity time of the late sown crops.

6.14.5 Diversification of Rice Based Crop Rotation

Reclamation of alkali soils following rice-wheat crop rotation increases infiltration rate, catchment retention, storage, along with decrease in run-off outflow (Singh et al. 1979). These improvements lead to favourable **water balance** in the area as compared to that where no reclamation has been undertaken. But in spite of these improvements, water table in these areas is receding. This is because rice requires high amounts of water for its production (Table 12.2). At many places, sugarcane crop is also being introduced; which is equally a high-water demanding crop. When one considers water balance (Singandhupe 1986; Fig. 6.15) during raising of a paddy crop, in states like Haryana, Punjab, Uttar Pradesh, and Rajasthan, India, it is observed that there is a serious deficit of rainfall in meeting the water needs of crop during early growth periods and near maturity. That deficit has to be met though groundwater (tube wells) or canal water causing big constraint on natural resources (Chhabra 2002). Due to this, in good quality water zones, water table is falling. This demands a rational control on existing and areas being expanded under rice and sugarcane crops in water-deficit zones to save groundwater.

To supplement income, the farmers can take summer bean (Green gram, *Vigna radiate*) or cowpea (*Vigna sinensis*), as *zaid* crops with short production cycle, during this period. These crops require only one irrigation and improve soil health by adding organic matter through leaf fall, fixation of atmospheric nitrogen and recycling of nutrients from lower depths to the top layers. Similarly, taramira (Rocket salad, *Eruca sativa*), a highly drought resistant short duration crop can be raised on residual moisture after rice and before late sown wheat crop.

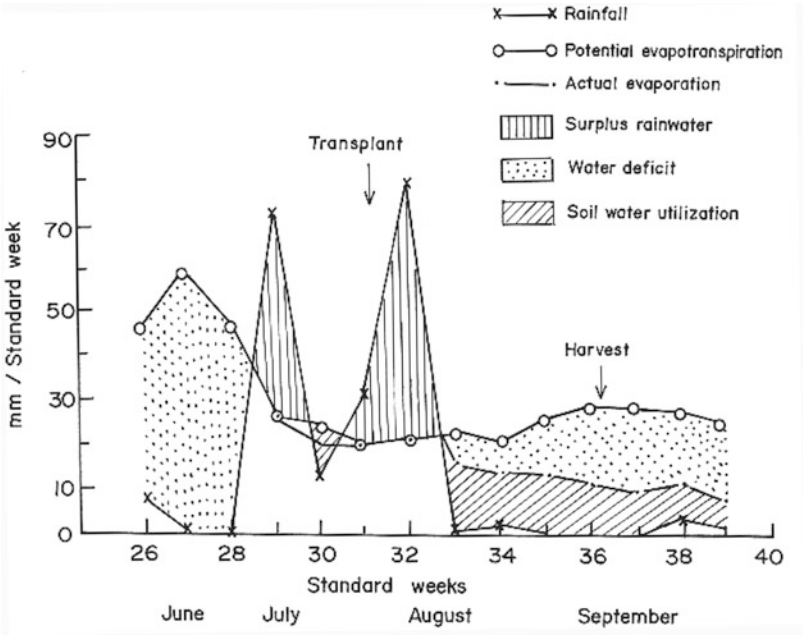

Fig. 6.15 Water balance for rice during growing season in an alkali soil in Haryana, India (Singandhupe 1986)

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